LABORATORY, SEMI-PILOT AND ROOM SCALE CONTROL OF H_2S EMISSION FROM SWINE BARNS USING NITRITE AND MOLYBDATE

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ABSTRACT

Emission of odorous and gaseous compounds such as hydrogen sulphide (H_2S) from livestock facilities can be a major impediment to its daily operations and potential expansion. Occupational and environmental concerns require the control of H_2S emissions. A treatment approach used in the oil industry in which nitrite and/or molybdate are used as metabolic inhibitors to control the production of H_2S in oil reservoirs was shown to be effective in controlling H_2S emissions from swine manure.

The addition of nitrite and molybdate to swine manure was investigated in closed laboratory scale systems and then evaluated in semi-pilot scale open systems and in specifically designed chambers aiming to simulate an actual swine barn. The effect of manure age (extent of storage) on H_2S emissions and the levels of nitrite and molybdate required for effective control of these emissions were assessed. Laboratory scale tests showed that emission of H_2S was dependent on manure age. Fresh manure emitted the highest level of H_2S and the level of emission decreased as manure age (1-6 months) increased. With fresh 1, 3, and 6-month old manures average H_2S concentration in the headspace gas of the closed systems were 4856±460, 3431±208, 1037±98 ppm, and non-detectable (<0.4 ppm), respectively. This translated to lower levels of nitrite or molybdate required to control H_2S emission with increase in manure age. When compared to molybdate, the addition of nitrite initially led to lower levels of H_2S but its effect was only temporary and not as persistent as molybdate. In the semi-pilot and room scale tests H_2S levels emitted from untreated fresh manure (831±26 ppm and 88.4 ppm, respectively), were significantly lower than those observed in the laboratory system (4856±460 ppm). Moreover, the levels of molybdate required to control the emission of H_2S were much

lower in both the semi-pilot system and in the room scale chamber than in the closed system (0.1-0.25 mM as opposed to 2 mM).

Small scale land application of manure treated with 0.1 mM molybdate did not raise the level of molybdenum in the soil that could cause potential toxicity to plants and animals. No major differences in the nutrient properties of the soils exposed to the treated and untreated manure were observed. Finally, a preliminary feasibility study of this treatment approach showed that the cost associated with this control approach was less than 1% of the total production cost.

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

1. INTRODUCTION

The swine industry has been constrained by the impact of odour and gaseous emissions from pig production facilities. This has adversely affected the acceptability and sustainability of swine operations. Swine production has increasingly shifted towards larger centralized operations housing a huge number of animals. Confining the animals also meant increased concentrations of airborne elements which could be injurious to both workers and animals (Thu, 2002). Among the emitted gases, ammonia (NH_3) and hydrogen sulphide (H_2S) are of major concern (Watts, 1999). Emitted H_2S originates from swine manure and is formed by dissimilatory reduction of sulphate carried out by sulphate reducing bacteria, as well as anaerobic degradation of sulphur-containing organic compounds, especially proteins (ASCE, 1989 and Arogo, et al., 2000). Exposure to hazardous levels of H_2S has been implicated in many fatalities and reported in various livestock operations (Curtis, 1983). In a study conducted by Chenard et al. (2003), H_2S concentrations as high as 1000 ppm were measured in certain swine operations. Under the Respiratory Protection Guidelines of the Canadian Centre for Occupational Health and Safety, H_2S at concentration of 100 ppm is considered immediately dangerous to life and health (IDLH) of humans (CCOHS, 2005). Further, exposure to 500-700 ppm H_2S for 30-60 minutes could cause loss of consciousness and possible death while at 800-1000 ppm H_2S could cause rapid unconsciousness, cessation of respiration and consequently death (ASABE, 2005b). Studies conducted by Thu (2002) revealed that neighbours to large-scale swine facilities are at an increased risk of respiratory tract infection and swine confinement workers have higher incidence of chronic bronchitis, occupational asthma, and organic dust toxic syndrome. With a density higher than air, H_2S also tends to accumulate in the poorly ventilated areas which exacerbate its

hazardous impact. In addition to its toxic and odorous nature, H_2S is corrosive and contributes to rapid deterioration of reinforced concrete and other construction components such as slatted floors and manure channels (Assaad et al., 2003). Due to the health and environmental concerns and stricter regulations associated with H_2S emissions, various approaches have been investigated to control the production and emission of H_2S from swine manures. These include application of various pit additives and chemicals to prevent the emission in situ (Barber and McQuitty, 1974; Clanton et al., 1999; McCrory and Hobbs, 2001; Tengman et al., 2001; Smith and Nicolai, 2005; Govere et al., 2005 and Shah et al., 2008), and utilization of biofilters to remove the H_2S from the emitted gases (DeBruyn, 2000; Nicolai and Janni, 2001a; and Nicolai and Janni, 2001b).

Biofilters which utilize the activity of microorganisms immobilized on media such as peat, compost or wood chips, are shown to be effective in treatment of emitted gases and H_2S (DeBruyn, 2000; Martinec et al., 2001; Nicolai and Janni, 2001b). However, use of biofilters is not widespread due to high operating costs associated with aeration, significant pressure drop, plugging of the biofilter as a result of biomass overgrowth (Riskowski, 2004), and difficulty in effective supply of the nutrients required by the microbial population and maintaining a good balance. The application of pit additives is a more common and commercially available method used to alleviate odor and gaseous emissions from livestock operations. These additives can be classified as masking agents, counteractants, digestive deodorants, absorbents, and chemical deodorants (Ritter 1989). The application of calcium hydroxide, ferric chloride, ferrous chloride, ferrous sulphate, hydrogen peroxide, potassium permanganate, sodium chlorite, ammonium persulphate, and sodium nitrate to control H_2S emissions from swine manure

have been studied in laboratory and farm scale systems achieving up to 90% in reduction of H_2S (Barber and McQuitty, 1975; Clanton et al., 1999; Smith and Nicolai, 2005). Tengman et al. (2001) evaluated 35 commercial additives, among which 10 were able to reduce H_2S emission with the reduction percentages varying in the range 14-47%. There is difficulty in determining which additive or combination of additives is most effective since the odour emitted from swine manure is complicated and thus needs in-depth classification with respect to the inherent characteristics of these odorous compounds (Zhu, et al., 1997). Moreover, additives are usually effective over a limited period and thus frequent application is required (McCrory and Hobbs, 2001).

Effectiveness of manure amendment with nitrite or molybdate as a means to control the emission of H_2S from swine manure has been investigated in a previous work (Predicala et al., 2008). This treatment approach has been developed originally in the oil industry for mitigation of oil reservoir souring (Hitzman et al., 1995; Nemati et al., 2001; Myhr et al., 2002; Greene et al., 2003). The approach utilizes nitrite and molybdate as metabolic inhibitor to hinder the activity of bacteria responsible for the production of H_2S. Using both laboratory (125 mL and 4 L) and semi pilot (200 L) scale systems, it was shown that addition of 80 mM nitrite or 2 mM molybdate could control the emission of H_2S from the fresh manure (Predicala et al., 2008). Most of the tests conducted in this study were done using fresh manure. Considering that livestock operations usually store the manure in large lagoons for up to six month prior to land application, the influence of the storage period on the extent of H_2S emissions and the corresponding levels of nitrite and/or molybdate required to treat this emissions needed to be investigated. Hence, in the present work, manure of different ages (extent of storage period), specifically fresh, 1-, 3- and 6-month old, were tested in closed laboratory scale systems. Since these tests were

conducted in closed systems, accumulation of the emitted gases in the headspace resulted in H_2S levels significantly higher than those expected in an open system which could have potentially led to overestimation of the required levels of nitrite and molybdate in a practical situation. Thus, the treatment approach was evaluated in semi-pilot scale open systems and in specifically designed chambers aiming to simulate an actual swine barn. Following the room scale (chamber) evaluation, manure analysis and small scale land application of manure was conducted to determine the impact of the treatment on manure properties and soil nutrient properties when treated manure is applied to land. Further, based on the finding of the room scale tests a feasibility study for treatment of manure with molybdate was conducted for an average size swine operation.

2. LITERATURE REVIEW

2.1. Background

Swine production has shifted to larger centralized confined production facilities during the rapid expansion of the swine industry in the past decade. This shift in production strategy has provided farmers with economic benefits in terms of management and labour efficiency, but it has also generated greater concerns with regard to public health and the environment. Enclosed production facilities emit large quantities of odorous and hazardous gases. Among the gaseous emissions from swine operations, ammonia and hydrogen sulphide are of major concern (Watts, 1999).

Hydrogen sulphide (H_2S) is a highly toxic gas which could potentially be fatal to human and animals at certain concentration levels. To address concerns associated with H_2S emissions, a number of studies have been conducted aiming to control H_2S, as well as other odour and gaseous emissions from the swine manure. These include the use of in situ (e.g. pit additives) and ex situ (e.g. biofiltration) methods of H_2S removal. The following section presents the various methods used to control H_2S emissions from swine manure as well as information on the nature, characteristics and production of H_2S in swine barns.

2.2. Swine manure production, characteristics and storage

Wastes from swine operations consist mainly of feces, urine and flushed water (usually from drinkers and from cleaning operations). Swine manure is estimated to constitute about 90% water and 10% solids when excreted by the animals (ASABE, 2005a). Based on its dry matter content, swine manure is classified as a slurry, which

contains about 4% to 10% solids (MWPS, 2004). The properties of manure depend on several factors, including diet composition and digestibility, animal age, environment, and stage of production (MWPS, 2004).

Pigs produce manure at different rates depending on the stage of their growth. Lactating sows (192 kg) typically produce the largest amount of manure among pig production groups with a rate per animal of 12 kg day^{-1}, while nursery pigs (12.5 kg) produce the least with a rate per animal of 1.33 kg day^{-1}. Grow-finish pigs (70 kg) produce manure at a rate per animal of 4.67 kg day^{-1} (ASABE, 2005a). These manure production rates are "as-excreted" values; the amount of manure that a waste handling system has to manage is usually much larger due to the addition of flushed water, spilled feeds, and dust, among others (MWPS, 2004).

In most commercial barns, pig pens are usually constructed with slatted floors above concrete-lined manure pits. The pits are used as temporary storage space of wastes. When full, emptying of the pits is done by pulling the plug capping the drain hole of the pit, therefore allowing the slurry to drain out of the production room by gravity into a transfer pit in a centralized collection area. From this transfer pit, manure is then pumped out into bigger outdoor manure storage structures and stored for a longer period of time (6 months or more). Once the outdoor storages are full, manure wastes are emptied and applied to crop fields mainly as nitrogen fertilizer.

2.3. Production of Hydrogen Sulphide from swine manure

Hydrogen sulphide is formed from manure in two ways: 1) by dissimilatory sulphate reduction and 2) by assimilatory reduction or anaerobic protein degradation.

Dissimilatory or respiratory sulphate reduction produces hydrogen sulphide through reduction of sulphate by activity of anaerobic sulphate reducing bacteria (SRB) under conditions favourable for their growth (ASCE, 1989). Sulphate reducing bacteria grow using a variety of organic compounds as energy source and electron donor and in so doing they utilize sulphate and other inorganic sulphur compounds as electron acceptors to form sulphide (Blunden, 2006). The sulphate content of manure, which is used by these bacteria, basically comes from the feeds and water that animals take in (Arogo et al., 2000). Organic compounds or hydrogen are used by SRB as electron donor in the reduction of sulphate to sulphide (Postgate, 1984). SRB are strictly anaerobic and belong either to the proteobacteria δ-subclass, gram positive bacteria branch (*Desulfotomaculum*, *Desulfosporosinus*), and the branches formed by *Thermodesulfobacterium* and *Thermodesulfovibrio* (ASCE, 1989; Rabus et al., 2006).

Hydrogen sulphide can also be produced through anaerobic degradation of proteins (Barber and McQuitty, 1974). As manure decomposes anaerobically, its organic sulphur portion decreases as proteins are broken down into amino acids such as methionine, cystine, and cysteine (Clanton and Schmidt, 2000). The amino acids are then further degraded to form sulphide. Amino acids are degraded through enzymatic action by heterotrophic bacteria, such as those of the genus *Proteus*, in a process called putrefaction (Barber and McQuitty, 1974).

2.4. Release of Hydrogen Sulphide from swine manure

Under normal conditions, most of the produced H_2S stays near the manure surface and is only released to the atmosphere when the manure is disturbed or agitated. The

release of H_2S from liquid swine manure was investigated by Ni et al. (2001). They proposed "bubble release" as the main mechanism that governs the release of H_2S with influence from convective mass transfer. The process of bubble release was explained by Ni et al. (2001). Once H_2S is produced, it dissolves in liquid manure and the continuous production of dissolved H_2S makes it supersaturated. This results in formation of micro air bubbles (MAB). Due to heterogeneity of manure, temperature difference, etc., movement of MABs is slow which induces collision and agglomeration of the MABs that result in larger air bubbles. When air bubbles reach a critical size, they gain in speed due to buoyant force, which moves them upward. This movement makes air bubbles absorb other MABs and larger air bubbles on their way toward the surface. The bubble size increases with the snowball effect and thus accelerates their upward speed. The bubbles eventually reach the manure surface and H_2S is released to the air. Ni et al. (2001) further proposed that bubble release is responsible for "H_2S burst releases", the sudden spikes in the release of H_2S by more than 100% as compared with previous release in less than one hour. Arogo et al. (1999) revealed that the release of H_2S from liquid manure into the air was sensitive to changes in liquid and air temperatures. They further implied that higher emission rate of H_2S could occur in a situation where the liquid temperature is higher than the air temperature. This was based on the observed increase of mass transfer coefficient when the difference between the two temperatures increased.

2.5. H_2S characteristics and associated problems

Hydrogen sulphide is a colourless gas which is slightly heavier than air (1.19 times higher at 20 °C and 760 mm Hg), highly soluble in water (at basic pH values) ,

flammable and corrosive (ASABE, 2005b, Lide, 2009). It is considered the most dangerous gas among the gases emitted from manure. Since H_2S is heavier than air, it tends to settle near the ground and can accumulate in enclosed, poorly ventilated, and low-lying areas (Schiffman et al., 2001). It has the characteristic odour of rotten egg at low concentrations (Curtis, 1983) but its odour is undetectable at higher concentrations, which makes it unknowingly dangerous. Its odour is barely detectable at 5 ppb but easily detectable at concentrations around 4 ppm (ASABE, 2005b). The H_2S odour does not give adequate warning because it paralyzes the olfactory system and thus diminishes the ability to detect the smell after a short period of exposure or to recognize greater degree of the odour at high concentrations (ASABE, 2005b). The loss of ability to smell H_2S begins at 50 ppm and the sense of smell may rapidly diminish (in 2-15 minutes) at exposures above 100 ppm (CCOHS, 2005).

Normally, H_2S remains within the manure slurry and is only released into the surrounding atmosphere when the manure is disturbed or agitated. Typical levels of H_2S inside swine buildings tend to range from 500 ppb to 2 ppm but can be much higher when manure is agitated (Schiffman et al., 2001). In a study conducted by Chenard et al. (2003) H_2S concentrations as high as 1000 ppm were observed during certain barn operations. Patni and Clarke (2003) were able to measure H_2S concentrations of up to 1300 ppm on slats of a grow-finish room during manure agitation by blowing air into the slurry with the use vacuum tankers. These potentially dangerous levels of H_2S are experienced in swine confinement buildings during the pulling of manure pit plugs, manure pump out, operation and maintenance of manure handling equipment and drainage lines, and power

washing (Christianson et al., 2004). Critical levels of H_2S could be more pronounced if ventilation in the building is not sufficient. Hydrogen sulphide concentration is usually below 1 ppm under normally ventilated buildings without manure agitation (Heber et al., 1997).

The toxicity of H_2S has been widely studied. It enters the body through the lungs mainly by inhalation and then dissolves in the blood and is carried throughout the body in the bloodstream. It affects breathing by causing the respiratory control centre in the brain to shut down which then stops the respiration and eventually cause death as oxygen in the blood is quickly used up, causing the heart to stop (Bhambhani and Singh, 1991). It has cyanide-like properties, which inhibit mechanisms in the oxidative phosphorylation and aerobic metabolism of the cytochrome oxidase systems in cells, causing oxygen deprivation or asphyxia (Gerasimon et al., 2007).

Due to the toxic effects of H_2S, exposure limits for humans have been established. Both the CCOHS and NIOSH (National Institute for Occupational Health and Safety, 2005) has set a recommended exposure limit of 10 ppm for up to 10 hours TWA (time weighted average) and a short-term exposure limit (STEL) of 15 ppm for 15 minutes. Furthermore, they have set the concentration of 100 ppm as immediately dangerous to life and death (IDLH) for humans. The purpose of establishing an IDLH value is to ensure that the worker leave a contaminated environment in the event of failure of most protective respiratory protection equipment. In the event of failure of respiratory equipment every effort should be made to exit immediately (CCOHS, 2005).

Human exposure to H_2S causes different effects at different concentration levels. Table 2.1 presents the different physiological responses of humans when exposed at

certain levels of H_2S. Respiratory problems include a series of overlapping conditions such as chronic bronchitis, occupational asthma, and organic dust toxic syndrome that have been documented to occur in up to 30% of swine confinement workers (Thu, 2002) At 30 ppm, H_2S becomes neurotoxic and induces nasal lesions in olfactory mucosa (Schiffman, et al., 2001). Chronic or acute occupational exposure to hydrogen sulfide concentrations near or above 500 ppm is known to result in Acute Respiratory Distress Syndrome (ARDS) or pulmonary edema among swine confinement workers, which can be fatal (Thu, 2002).

Table 2.1. Effects of hydrogen sulphide on humans at various concentrations of exposure (ASABE, 2005b).

Concentration (ppm)	Effect on humans
0.005	Barely detectable
4	Easily detectable, moderate odour
10	Eye irritation
27	Unpleasant odour
100	Coughing, eye irritation, loss of smell after 2–15 min exposure
200-300	Eye inflammation and respiratory tract irritation after 1 h
500-700	Loss of consciousness and possible death in 30–60 min
800-1000	Rapid unconsciousness, cessation of respiration and death
1000	Diaphragm paralysis on first breath, rapid Asphyxiation

As with humans, animals are also affected when exposed to H_2S. Pigs are made uncomfortable by prolonged exposure to low levels of H_2S. Pigs exposed continuously to at least 20 ppm develop fear of light, loss of appetite, and nervousness while continuous exposure to 50-240 ppm causes nausea, diarrhea, severe distress, eye irritation and

drooling (ASABE, 2005b). In acute poisoning, H_2S acts so rapidly that there are few symptoms of imminent danger. Sudden nausea and unconsciousness are followed by death at concentrations of 800 ppm or above (ASABE, 2005b). In addition to its toxic and odorous nature, H_2S is also corrosive. It contributes to rapid deterioration of reinforced concrete and other construction components such as slatted floors and manure channels (Assaad et al., 2003). Moreover, H_2S is also considered an extremely flammable gas, although its ignition temperature is relatively high at 260 °C (CCOHS, 2005).

2.6. Strategies used to reduce H_2S missions

Several methods have been investigated aiming to eliminate or at least reduce emission of hydrogen sulphide to levels below the critical limits. Some approaches have been adopted by the industry while some need further research. These methods are discussed in the following sections.

2.6.1. Methods that control emitted H_2S from manure

2.6.1.1. Biofiltration

Biofiltration is a biological process in which a reactor packed with a matrix wherein a biofilm containing a suitable microbial population is formed (Mahmood et al., 2007). Biofilters use microorganisms to break down gaseous contaminants and produce end products such as biomass, CO_2 and water. They use a porous solid medium to support the growth of microorganisms and allow access to the contaminants in the flowing air. Odorous compounds are absorbed in the filter media where they are oxidized by resident microorganisms (DeBruyn, 2000). Most biofilter media are composed of various proportions of biological residues, such as compost, peat, and soil, and bulking

agents which include wood chips, heather, and synthetic material (Nicolai and Janni, 2001a).

Several studies have reported the effectiveness of biofilters in controlling H_2S emissions. Yang and Allen (1994) were able to achieve H_2S removal from waste gas with 99.9% efficiency for inlet concentrations in the range from 5 to 2650 ppm using biofilter with waste compost as packing material. A study conducted by DeBruyn (2000) in a 2000-head hog facility in Manitoba resulted in reduction of H_2S and NH_3 emissions of 56 to 100%, with the use of wood chips and compost as filter media. It should be noted though that during their tests, H_2S concentrations before entering the biofilter were relatively low ranging from 0.32 to 1.1 ppm. In a similar study, an average reduction rate of 87% was found by Nicolai and Janni (2001b) with a biofilter using a mixture of wood chips and compost with high moisture content. They recommended a mixture of 30% compost and 70% wood chips to avoid significant pressure drop across the biofilter. Chang et al. (2004) tested a biofilter using a mixture of pine chaff and perlite as filter media and were able to reduce H_2S and odour levels by 82.4% (inlet conc 20-60 ppm). Odour emissions were also reduced by 61-75% using a biofilter with biochips (test material from the company Roth GmbH, Oberteuringen, Germany) and coconut fibre peat as filter media (Martinec et al., 2001).

Even with the promising results, the use of biofilter in reducing emissions from swine operations has not been well adopted. The main downside of using biofilters is the high operating costs associated with supply of air due to the significant pressure drop across the filter media (Green at al., 2005; Nicolai and Janni, 2001b; Riskowski, 2004). Another limitation in application of biofilters for swine facilities is the bedding size

required to treat the large air flow rates leaving the barn ventilation system and the short retention time (Lemay, 1999). Further, careful selection and management of the media is required to ensure provision of sufficient environmental and nutritional requirements such as moisture, temperature, and nutrients for microbial growth (Nicolai and Janni, 2001a).

2.6.1.2. **Bioscrubbing**

Bioscrubbers remove H_2S from contaminated streams by absorption of H_2S in a liquid, usually water or an alkaline solution followed by biological oxidation of H_2S in the liquid (Syed et al., 2006). Bioscrubbers are relatively similar to biofilters. In a bio-scrubber, the exhaust air is washed with a recycled liquid, usually water, before biological oxidation (Lemay, 1999). In a study conducted by Nishimura and Yoda (1997) 99% of the H_2S, at concentrations of 2000 ppm, was removed from biogas produced from an anaerobic wastewater treatment process using a multiple bubble-tray airtight contact tower that scrubbed H_2S from the biogas. A fixed-film bioscrubber containing a mixed culture of *Acinetobacter* sp. MU1-03 and *Alcaligenes faecalis* MU2-03, isolated from a municipal wastewater treatment plant, was able to remove 98% of the H_2S from a gas stream (Potivichayanon, et al., 2006). A bioscrubber consisting of an endless polypropylene screen running in a trough of alum solution was evaluated by Shah et al. (2008) with the goal to reduce emissions from a pig finishing house. The bioscrubber was able to reduce NH_3 emissions by 58.3% over more than 66 hours of evaluation. Similar to biofilters, the use of bioscrubbers in reducing H_2S and odour emissions from swine barns

needs further evaluation to tackle the concerns regarding pressure drop, large footprint, and capital and maintenance costs (Shah et al., 2008; Lemay, 1999).

2.6.2. Methods to prevent generation of H_2S from manure

2.6.2.1. Diet manipulation

According to Watts (1999), diet manipulation can potentially reduce H_2S emissions in two different ways. First, by adopting more digestible diets, manure production and consequently odour emissions can be reduced when waste decomposes. Second, by altering the chemical composition of the diet the quantity and characteristics of the odours produced subsequently are changed. Much of diet manipulation studies have focused toward reducing H_2S concentration by reducing crude protein contents and mineral sources of sulphur (Powers, 2004). It has been reported that most odorous compounds, including H_2S, are associated with amino acid degradation (Sutton, et al., 2006). Altering the protein content, and consequently the amino acid composition of the diet to match the amino acid content of diets to the animal's needs will reduce excretion of excess nutrients and consequently the potential for odour generation (ASABE, 2007).

A study by Kendall et al. (1999) showed that reducing crude protein (CP) by 4.5% and adding synthetic amino acids to pig diets reduced H_2S emissions by 40%. In a subsequent study, Kendall et al. (2001) used a diet formulated with reduced dietary CP (by 3.25%) with 5% added soybean hulls and a non-sulphur trace mineral premix with highly available P corn (low nutrient excretion diet) and were able to lower H_2S emissions by 43.4%. Shurson et al. (1999) formulated low sulphur diets and results showed reduction of total sulphur and sulphate excretion by 30% which subsequently

reduced H_2S emissions. In a study by Hill et al. (2001), 32% reduction of H_2S in room air was achieved by adding 10% soy hulls with 3.4% fat to corn-soybean meal diets. Other studies on diet manipulation, aiming to reduce H_2S emissions, include the use of proteolytic enzymes to improve protein digestibility, use of dietary supplements as odour absorbers and the use of plant extracts, enzymes, and direct-fed microbials as feed additives (Watts, 1999).

Feed manipulation techniques to reduce H_2S and odour emissions from swine manure have not been widely adopted mainly due to economic issues. Additionally, more practical field studies are required to confirm results and environmental benefits and also to determine the cost of new diet modifications (Sutton, et al., 2006).

2.6.2.2. Oil sprinkling

Originally**,** oil sprinkling was mainly employed to control dust and particle emissions inside swine barns by coating surfaces with vegetable oil (Powers, 2004). Studies have shown that oil sprinkling does not only control dust emissions but it could also reduce H_2S emissions. Ouellette et al. (2006) reported that oil sprinkling can reduce odour and H_2S emissions through the removal of dust which potentially serve as "odour carriers". Odorous compounds emitted into the air typically bond to airborne dust particles and therefore removed when these suspended dust particles are removed.

An experiment was conducted by Zhang (1997) at the Prairie Swine Centre with the use of canola oil sprinkled on one grow-finish room in variable dosages averaging 6 millilitres per square meter of floor area. Results of the study revealed reduction of H_2S concentration by 27% over a 1-year experiment period. Jacobson et al. (1998) reported reduction of H_2S emissions by up to 60% by sprinkling soybean oil at a rate of 0.5

mL/ft^2. An oil/water sprinkling system was evaluated by Paszek et al. (2001) to reduce odour emissions from deep-pitted, curtain-sided finishing buildings. Their study showed significant reduction of H_2S (initial levels ranging from 32.5-1500 ppb) as well as odour and NH_3 emissions in rooms sprinkled with oil at an average rate of 6.7 mL/m^2-day when compared with control rooms. Kim et al. (2008) also showed significant reduction of H_2S (mean initial level of 37.7 ppb) for 24 hours after spraying with an essential oil (mixture of herb and ravenda). They further indicated that the essential oil functioned not only as a masking agent but also as an antimicrobial agent. Contrary to these results, studies conducted by Godbout et al. (2001) with canola oil and those performed by Ouellette et al. (2006) using soybean, canola, and sunflower oils showed no reduction of H_2S emissions.

A study was conducted by Huang et al. (2004) aiming to evaluate several odour management techniques in terms of their cost effectiveness. The techniques evaluated were evaporative misting, wet scrubbing, automatic oil sprinkling, diffusion-coagulation-separation (DCS) dedusting, manual oil sprinkling, draining shallow pit systems once a week and increasing floor space allowance per pig. Among the 9 techniques reviewed, automatic oil sprinkling ranked first with a cost of $0.51/marketed hog. Oil sprinkling incurs relatively minimal operational costs but involves safety issues such as the slippery conditions of pens and alleys following repeated oil applications (Powers, 2004). This would generate a safety hazard for barn personnel and could result in injuries thereby negating its purpose of creating a safe and odour free environment. In addition, oil sprinkling requires careful attention so that the areas near fans, heaters, and surrounding feeders are not affected, as oil could interfere with equipment operation. This would also

require additional cleaning and maintenance to prevent oil contamination and build upon these equipment (Schmidt and Heber, 2004).

2.6.2.3. Pit additives

Application of manure pit additives is one of the earliest methods used to alleviate odour and gaseous emissions from livestock operations. Pit additives are substances applied to the manure with the intention of mitigating odour and gaseous emission problems associated with it (McCrocy and Hobbs, 2001). Pit additives can be classified as masking agents, counteractants, digestive deodorants, absorbents and chemical deodorants (Ritter 1989).

According to ASABE (2007), masking agents are mixtures of volatile oils that have a stronger odour than the manure, and are designed to cover-up the objectionable odour with a more acceptable odour. Deodorants on the other hand are products that are used to eliminate or transform the odorous constituents in the manure so that they are not emitted. They are strong oxidizing agents or chemicals that may inhibit the microbial activities, or alter the digestive process by changing enzyme balances, or simply change the chemistry of odorous compounds by changing the pH of the manure. Counteractants are compounds that have the odour characteristics appropriate to cancel the manure odours so that the total intensity detected is less than that of the mixture of the counteractants and manure, while adsorbents are agents with large surface areas that could be used to adsorb the odours before they are released to the environment.

Certain chemicals control the emission of odour and gases through modification of pH or oxidation of odour causing compounds. According to McCrocy and Hobbs

(2001), oxidizing agents decrease odour concentration in the manure and inhibit the formation of odourants by the indigenous microorganisms. Barber and McQuitty (1975) reported that ammonium persulphate, potassium permanganate and sodium nitrate were effective in control of sulphate reducing bacteria and biogenic sulphide production. Clanton et al. (1999) used calcium hydroxide, ferric chloride, ferrous chloride, ferrous sulphate, hydrogen peroxide, potassium permanganate, and sodium chlorite to control H_2S emissions from swine manure in the laboratory scale systems and were able to achieve 90% decrease in H_2S emission when these chemicals were applied at quantities above 0.6, 1.0, 0.25, 0.3, 0.01, and 0.45 g/g dry manure, respectively. Application of potassium permanganate and hydrogen peroxide in a farm scale swine manure pit reduced the level of emitted H_2S by 90% a few minutes after addition (Smith and Nicolai, 2005). Yokoyama et al. (2006) evaluated the use of boric acid and sodium tetraborate for their ability to inhibit NH_3 and H_2S emissions from swine wastewater and manure slurry in in vitro incubations. The $NH_3$and H_2S emissions were eliminated from wastewater and manure slurries through addition of either 1% boric acid or sodium tetraborate over 7 days of incubation. Additionally, the use of minced horseradish with calcium peroxide or hydrogen peroxide has been reported to reduce odour intensity and unpleasantness from swine manure (Govere et al., 2005).

Various additives are available commercially but none of them has been proven to be totally effective. There is difficulty in determining which additive or combination of additives is most effective since the odour emitted from swine manure is complicated and thus needs in-depth classification with respect to the inherent characteristics of these

odorous compounds (Zhu, et al., 1997). Moreover, additives are usually effective over a limited period and thus frequent application is required (McCrory and Hobbs, 2001).

Tengman et al. (2001) reported an evaluation study of 35 commercial additives conducted by Purdue University Agricultural Air Quality Laboratory. Each product was tested three times (42 days each replicate) in an enclosed 15-inch diameter by 48-inch tall manure storage reactor. Among the additives tested, only 10 were able to reduce H_2S concentration with rates ranging from 14-47% and with 75-95 % certainty of decrease. With a 75% confidence level, it could be expected that one out of four times, the same results could be achieved without any effect from the product. Stinson (1999) also evaluated 3 commercial additives under actual barn conditions and achieved H_2S reductions of 14 to 76%. Various commercial additives have shown to be significantly effective in reducing H_2S emissions, however they usually incur considerable cost both in material and manner of application.

While the idea of using pit additives to reduce odour is very attractive, the efficacy of these additives seems questionable. It is difficult to assume that pit additives will show the same results in commercial scale conditions as they would under laboratory conditions (Lemay, 1999). It is advised to conduct careful laboratory and field evaluations of commercial additive products before they are adopted for abatement of H_2S and odour emissions in commercial scale (ASABE, 2007).

2.6.2.4. Microbial treatment of H_2S in other environments

The health and environmental issues associated with the biogenic production of H_2S is not a concern only in livestock operations but also in other industrial and

agricultural operations such as in oil production and processing and in pulp and paper plants (Tang et al., 2009). The bacterial production of H_2S in oil reservoirs subjected to water flooding (souring) is a major concern in the oil industry since H_2S affects the quality of produced oil and gas (Hubert et al., 2003). It also causes corrosion of pipelines and production and processing equipment and decreases the efficiency of secondary oil recovery (Tang et al., 2009). More importantly, the greater concern for H_2S production in the oil industry is the health risk to workers brought about by the toxicity of H_2S. To address these concerns, the oil industry has taken various steps to suppress or at least reduce the production of H_2S in oil reservoirs.

Strategies for control of souring in oil reservoirs include the application of biocides such as glutaraldehyde and diamine and amendment of injection water with molybdate, nitrite, nitrate or a combination of nitrate and nitrate-reducing, sulphide-oxidizing bacteria (Gardner and Stewart, 2002; Hubert et al., 2003; Hubert and Voordouw, 2007; Myhr et al., 2002; Nemati et al., 2001; Reinsel et al., 1996; Telang et al., 1998). Although biocides were shown to be effective in controlling souring and biocorrosion, their efficiency could be reduced when the SRB present is protected in a biofilm (Gardner and Stewart, 2002). Further, frequent biocide application, especially at low doses, could also cause emergence of resistant strains of SRB (Telang et al., 1998). Scouring can also be prevented and remediated by injecting nitrate into oil reservoirs. Nitrate has the ability to stimulate nitrate-reducing, sulfide-oxidizing bacteria and heterotrophic nitrate-reducing bacteria which the former has the ability to oxidize and remove H_2S, while the latter could compete with SRB and outcompete these bacteria which are responsible for production of H_2S in the first place (Hubert and Voordouw,

2007). Nitrite on the other hand has strong inhibitory effect on SRB and production of H_2S. Reinsel et al. (1996) showed that application of 0.71 mM nitrate (as nitrogen) and continuous addition of 0.71-0.86 mM nitrite were able to successfully suppress microbial scouring in crushed Berea sandstone columns with oil-field produced water. Microbial production of H_2S in seawater-flooded oil reservoir model column was also completely eliminated by injection of 0.5 mM nitrate for 2.5-3.5 months (Myhr et al., 2002). Hubert et al. (2003) conducted an experiment to contain the biogenic production of H_2S in a continuous up-flow packed-bed bioreactors simulating oil reservoir biological conditions with the addition of either nitrate or nitrite. The production of H_2S by SRB was prevented by addition of 17.5 mM nitrate or 20 mM nitrite. Nemati et al. (2001) also investigated the use of sodium nitrite and ammonium molybdate, as metabolic inhibitors on the production of H_2S by a pure culture of the sulphate-reducing bacterium (SRB) *Desulfovibrio* sp. strain Lac6 and a consortium of SRB, enriched from produced water of a Canadian oil field. They found that addition of 0.1 mM nitrite or 0.024 mM molybdate at the start of growth prevented the production of H_2S by SRB. Moreover, they identified a synergistic effect in simultaneous addition of nitrite and molybdate. The use of nitrite and molybdate was shown to be a promising technique in controlling the production of H_2S from oil reservoirs.

2.6.2.5. Use of nitrite and molybdate to control H_2S emission from swine manure

The microbiology, physicochemical and environmental conditions in oil reservoirs may be different from that of manure pits, but the activity of SRB seems to be the main cause of the production of H_2S in both cases. With the success in controlling

H_2S production in oil reservoirs through addition of nitrite and/or molybdate same method was adapted by Predicala et al. (2008) in controlling H_2S emissions from swine manure. They employed the technique of using nitrite and molybdate as metabolic inhibitors to hinder metabolic activity of the bacteria present in the manure which is responsible for production of H_2S.

The technique was tested in laboratory scale closed systems and then in semi-pilot scale systems. In the laboratory scale systems, tests were conducted in closed 125-mL serum bottles filled with 30 mL of fresh swine manure slurry. The manure samples were collected from a swine production room at the Prairie Swine Centre Inc, (PSCI) facility in Saskatoon, Canada. Specified amounts of nitrite and molybdate were added to the manure to reach final concentrations of 5, 10, 20, 30 and 40 mM for nitrite and 0.25, 0.5, 1.0, 1.5, 2.5, 3 and 4 mM for molybdate. Bottles containing manure without nitrite or molybdate addition were used as control. The effect of individual and combined addition of nitrite and molybdate were also investigated in these tests. The concentration of H_2S in the headspace gas of the bottles was analyzed using a gas chromatograph.

A summary of the results of the tests are presented in Tables 2.2 and 2.3. Table 2.2 shows the reduced and residual concentration of H_2S in the bottles applied with the various amounts of nitrite or molybdate separately, while Table 2.3 shows the concentrations in the bottles treated with combined nitrite and molybdate. The immediate concentration refers to H_2S concentration observed right after addition of the reagents (i.e., within 2 days after addition), while the residual concentration refers to final concentration observed at the end of the tests (12-65 days after addition). In the case for the control, the immediate and residual concentrations have been measured at the same time as treated bottles. It was observed that the individual addition of nitrite or molybdate initially decreased the concentration of H_2S to a lower level than in the control. However,

the concentrations in the bottles treated with all levels of nitrite and 0.25-0.5 mM molybdate started to increase two days after addition and eventually matched the same level as in the control (which reached above 1700 ppm, the upper limit of accurate measurement of H_2S reported in this work). The reduced level of H_2S (<12 ppm) in the bottles treated with 1.5, 2.5, 3.0, and 4.0 mM molybdate was maintained during the remaining part of the tests. This finding suggested that although both nitrite and molybdate reduced H_2S concentration immediately after application, molybdate has a more persistent effect in keeping a low concentration for a longer period of time. It could also be possible that higher levels of nitrite (> 40 mM) need to be used to maintain a reduced level of H_2S.

Table 2.2. H_2S concentration in the headspace gas of control and treated serum bottles containing fresh manure added with various amounts of nitrite and molybdate individually (Predicala et al., 2008).

Treatment	Immediate concentration[a] (ppm)	Residual concentration[b] (ppm)	Treatment	Immediate concentration (ppm)	Residual concentration[c] (ppm)
Control	1200	1700	0.25 mM Mo	265	1700
5 mM NO_2	1100	1700	0.5 mM Mo	65	1700
10 mM NO_2	500	1700	1.0 mM Mo	<12	1000
20 mM NO_2	300	1700	1.5 mM Mo	<12	50
30 mM NO_2	150	1700	2.5 mM Mo	<12	<12
40 mM NO_2	75	1700	3.0 mM Mo	<12	<12
			4.0 mM Mo	<12	<12

a – within 2 days after treatment, b – 12 days after treatment, c – 40 days after treatment

Table 2.3. H_2S concentration in the headspace gas of serum bottles containing fresh manure added with various amounts of nitrite and molybdate in combination (Predicala et al., 2008).

Final concentration of nitrite and molybdate in manure	Simultaneous addition		Subsequent addition	
	Immediate concentration[a] (ppm)	Residual concentration[b] (ppm)	Immediate concentration[a] (ppm)	Residual concentration[b] (ppm)
40 NO_2 x 0.5 Mo	<10	1240	<10	1500
40 NO_2 x 1.0 Mo	<10	1500	<10	1300
40 NO_2 x 2.0 Mo	<10	120	<10	60
80 NO_2 x 0.5 Mo	<10	500	<10	750
80 NO_2 x 1.0 Mo	<10	28	<10	100
80 NO_2 x 2.0 Mo	<10	18	<10	100

a – within 2 days after treatment, b – 65 days after treatment

The combined addition of nitrite and molybdate resulted in lower immediate H_2S concentration and was more persistent in keeping the concentrations low throughout the experiment when compared with the effect of nitrite and molybdate added individually (Table 2.3). All nitrite and molybdate combinations were able to reduce H_2S concentration to below 10 ppm immediately after addition. However, the concentrations started to rise again after two days. Only the addition of 40 mM nitrite and 2 mM molybdate, 80 mM nitrite and 1 mM molybdate and 80 mM nitrite and 2 mM molybdate maintained H_2S at low levels. As reported by Predicala et al. (2008), there was no difference in the H_2S profiles between simultaneous and subsequent addition of nitrite and molybdate. The initial addition of nitrite and subsequent addition of molybdate was conducted to validate the principle that H_2S concentrations are reduced to very low levels by nitrite and then maintained at these low levels by molybdate for a longer period of time. Again, as presented earlier, higher levels of nitrite (>40 mM) and molybdate (>2 mM) in combination could prevent spikes of H_2S and be able to maintain the low levels achieved immediately after addition for a longer period (>60 days).

Another set of serum bottles tests was also conducted by Predicala et al. (2008) but this time with aged manure (5-6 weeks old). Only nitrite treatments were used in

these tests. As with the fresh manure, the concentration of H_2S in the control started around 1200 ppm and then eventually increased above 1700 ppm at the end of the test period. Addition of 2 mM nitrite was not effective in treating H_2S with residual concentration of about 1200 ppm. On the other hand, the addition of 5 and 10 mM achieved low H_2S levels and maintained them throughout the test period (20 days after treatment). The effect was more pronounced with 10 mM nitrite added, with residual H_2S concentration of 70-90 ppm. With fresh manure, this residual level of H_2S was achieved by the addition of 40 mM. As reported by Predicala et al. (2008), this finding implies that the aging of manure could possibly reduce the amount of nitrite or molybdate required to control the emission of H_2S. The observed effect needs further investigation since these tests were conducted only with 5-6 weeks old manure aged manure. Furthermore, the effect of manure age on the required levels of molybdate for controlling H_2S needs to be explored, since molybdate was more effective in maintaining a low level of H_2S over a prolonged period. Examining the effects of simultaneous nitrite and molybdate addition in combination with manures of different age is also important. It would provide a more definitive trend and comparison on the levels of H_2S produced and treated. Moreover, it will also give the opportunity to look into the extent of H_2S emissions from manure stored for different periods of time in actual barns.

Similar findings from the serum bottle tests were also observed by Predicala et al. (2008) in 4-L narrow mouth bottles containing 1.5 L of fresh manure. Concentration of H_2S in the control bottle ranged from 1000 to 1400 ppm throughout the test period (9 weeks). The addition of 80 mM nitrite, 40 mM nitrite and 2 mM molybdate or 80 mM nitrite and 2 mM molybdate were effective in reducing and maintaining H_2S at levels

below 100 ppm throughout the test period. Following the positive results from the laboratory scale tests, nitrite and molybdate were also used to reduce H_2S emissions from swine manure in semi-pilot scale systems. Four cylindrical vessels of approximately 200 L in capacity were used for these tests. Each vessel was fitted with a lid with inlet and sampling ports for addition of the treatment agents and sampling of the headspace gas. One of the vessels was used as control without any treatment. The remaining vessels were applied with the treatments, namely; 80 mM nitrite, 2 mM molybdate and a combination of 80 mM nitrite and 2 mM molybdate (final concentrations in the manure slurry). These treatment levels were determined based on the laboratory scale experiment findings.

The average concentration of H_2S in the headspace gas of the semi-pilot scale systems before the treatment was found to be 533 ppm with a standard deviation of 28 ppm. The treatments were then applied and H_2S levels in the vessels were monitored for up to 17 days. Starting on day 8, the concentration of H_2S in the control vessel sharply increased from 550 ppm to 1450 ppm on day 15 and then slightly went down to 1200 ppm on day 17. These levels are comparable to the H_2S concentrations obtained in the laboratory scale experiments. As for the treated vessels, the addition of 80 mM nitrite, 2 mM molybdate or combination of 80 mM nitrite and 2 mM molybdate all reduced H_2S concentration within 24 hours after application. The decrease in H_2S levels was more pronounced when 2 mM molybdate or combination of 80 mM nitrite and 2 mM molybdate were used. No significant spikes of H_2S were observed in all the treated vessels and very low levels (<25 ppm) were maintained throughout the test period. The treatments were shown to be effective in reducing H_2S emissions but not with NH_3. All

the treated vessels showed the same levels of NH_3 with the control having concentrations ranging from 10 ppm to 100 ppm. With regards to odour levels, the vessels applied with nitrite and combination of nitrite and molybdate were observed to have lower odour concentrations (<8000 OU m^{-3}) than those in the control vessel and the one applied with molybdate only (around 11000 OU m^{-3}).

The findings by Predicala et al. (2008) revealed that the addition of nitrite or molybdate, a containment strategy commonly used to tackle the problem of souring in oil reservoirs, can be used in treating H_2S emissions from swine manure in the laboratory and semi-pilot scale systems. In the laboratory scale experiments, the addition of 80mM nitrite or 2mM molybdate reduced the emission of H_2S from fresh swine manure to a negligible level. The same result was obtained with aged manure but with only 10 mM of nitrite. One of the shortcomings in this study was the maximum detectable level of H_2S which was limited to 1700 ppm. Determining the full extent of H_2S emissions is essential to have a perspective of the magnitude of H_2S that can be emitted from swine manure and therefore understand better the effectiveness of nitrite and molybdate. Further, initial results from their tests showed that the amount of nitrite or molybdate required to control H_2S could be reduced when emission from aged manure (5-6 weeks old) was investigated. Considering that livestock operations usually store the manure in large lagoons for up to six months or more prior to land application, the influence of the storage period on the extent of H_2S emissions and the corresponding levels of nitrite and/or molybdate required to treat this emissions needed to be investigated. Additionally, Predicala et al. (2008) conducted these tests in closed systems in which accumulation of the emitted gases in the headspace resulted in H_2S levels significantly higher than those expected in an open system. This could have potentially led to overestimation of the

required levels of nitrite and molybdate. The treatment approach, thus, needed to be investigated further in open and larger scale systems comparable to real swine barn situations. Room scale setup that could simulate swine production conditions would provide the opportunity to test nitrite and molybdate in reducing H_2S emissions from swine manure in commercial scale.

3. KNOWLEDGE GAPS AND OBJECTIVES

Diet manipulation, oil sprinkling and use of pit additives are some of the typical approaches which have been investigated by other researchers to control the emission of H_2S from swine manure. Although some of these approaches show potential in reducing H_2S emissions from swine manure, they involve setting up complex installations and more importantly incur high capital and operating costs. Addition of nitrite and molybdate is used by the oil industry as an effective strategy to control the production of H_2S in oil reservoirs (Nemati et al., 2001). An earlier study by Predicala et al. (2008) has proved the effectiveness of this method on permanent control of H_2S emission from swine manure in laboratory and semi-pilot scale closed systems. However, the previous work did not investigate the effects of manure age or storage period on the extent of H_2S emission and the required level of nitrite and molybdate. Furthermore, the practicality of this approach for large scale livestock operations depends on confirmation of effectiveness in large scale trials. The treatment approach therefore needs to be investigated in semi-pilot and room scale open system so that its effectiveness and its economic feasibility can be assessed. Moreover, the potential safety and environmental issues which may arise from the treatment of manure need to be assessed prior to any practical application of the treated manure to crop lands as fertilizer.

The overall goal of this study was to control H_2S emissions from swine manure using an approach which utilizes nitrite and molybdate as chemical inhibitors to hinder metabolic activity of the bacteria present in the manure (responsible for production of sulphide) and as catalysts for spontaneous oxidation of the sulphide already present in the system. The overall approach of the study is outlined in Figure 3.1. Specifically, this study aimed to:

1. Assess the effects of manure age, specifically fresh, 1, 3, and 6 months, on the extent of H_2S emissions and the required amounts of nitrite and molybdate to control these emissions in closed laboratory scale systems.
2. Evaluate the treatment approach in semi-pilot scale open systems and in specifically designed rooms aiming to simulate an actual swine barn.
3. Evaluate the feasibility and economic aspects of the treatment approach.
4. Conduct preliminary study on the impacts of the treatment on the manure properties and its nutritional values as a fertilizer.

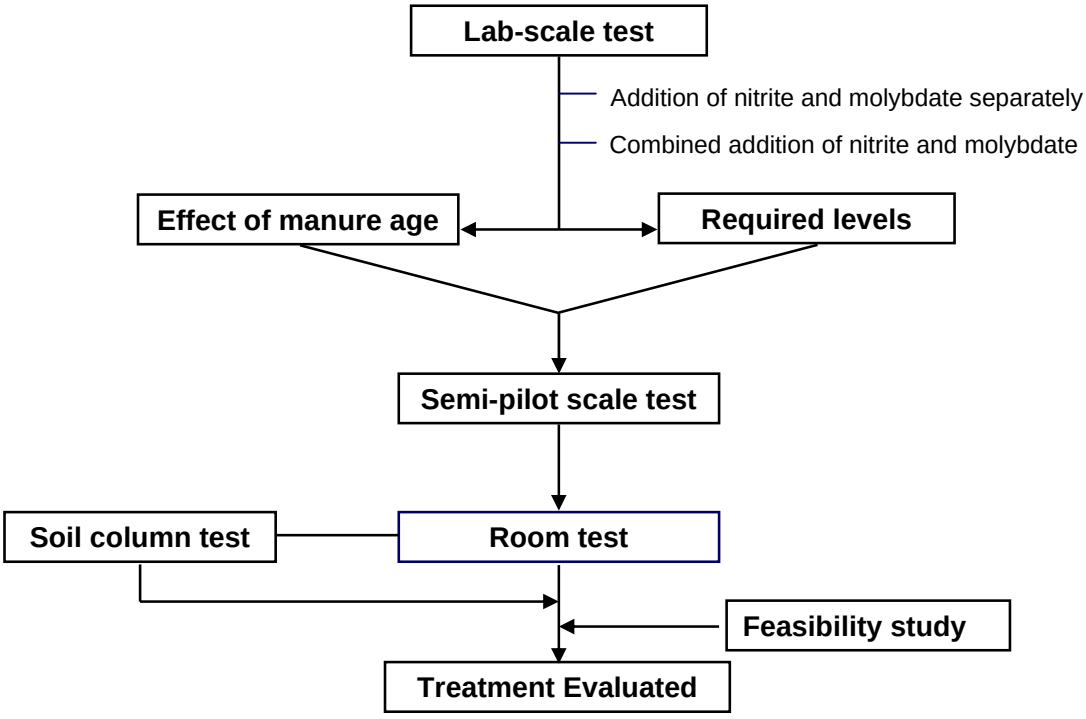

Figure 3.1. The overall approach employed in conducting the study.

4. MATERIALS AND METHODS

4.1. Laboratory scale tests

4.1.1. Manure sample preparation

The manure samples used in the experiments were collected from grow-finish rooms in the swine barn facility of the Prairie Swine Centre Inc. (PSCI), Saskatoon, Saskatchewan, Canada. The grow-finish stage of production refers to the 14 to 16-week period of raising the pigs coming out of the nursery (at about 15-20 kg) up to market weight of about 115-120 kg. To determine the effect of manure age on the extent of H_2S emission and the amount of nitrite and molybdate required to control these emissions, different ages of manure were investigated. Fresh, 1, 3, and 6-month old manures were used in the experiment. Fresh manure refers to manure accumulated over a period of two weeks in a previously cleaned underfloor manure collection pit of the selected grow-finish room. Manure in the pits was produced from pigs fed with standard commercial grow-finish diets. In collecting the samples, the area of the manure pit from which the sample was collected was mixed sufficiently to ensure homogeneity of the sample. Manure was scooped from the pit and placed in a clean bucket (19 L volume) using a shovel. To prepare the aged manure samples, the closed bucket containing the fresh manure was left undisturbed in a dark area at 20 °C for 1, 3, and 6 months. The aged manure samples were obtained by storing the same batch of manure collected fresh. Once the storage time of the manure was reached, a 2-L subsample was taken and screened using a coarse wire strainer to remove foreign materials such as spilled feed, worms and insects. The collected samples were then brought to the laboratory for the experiments.

Following the procedure used in the previous study of Predicala et al (2008), 125-mL serum bottles were filled with 30 mL of each type of manure sample and sealed with aluminium cap with septum. Several replicate bottles were prepared as needed for the various experimental treatments. It should be noted that no data from 6-month old manure are presented since H_2S readings from this manure were below the detection limit (<0.4 ppm).

Nitrite and molybdate treatments

Various concentrations of nitrite, molybdate and combination of nitrite and molybdate as listed in Table 4.1 were tested. A specified volume of a concentrated solution of nitrite (0.2 to 2.2 M $NaNO_2$ depending on the required final concentration) and/or molybdate (0.35-0.6 M $Na_2MoO_4.2H_2O$) was injected into the serum bottles to achieve the desired final concentrations. The amounts of nitrite and molybdate solutions applied to the manure to attain their final concentration are shown in Table 4.2. Control tests were also conducted using bottles containing manure slurry without any added nitrite or molybdate.

The concentrated solutions of nitrite and molybdate were prepared by diluting specified amounts of nitrite and molybdate salts in reverse osmosis (RO) water. The calculations in determining the amount of salts to be diluted in RO water to obtain a concentrated solution of nitrite or molybdate are presented in Appendix A.1. Correspondingly, the calculations in determining the amount of nitrite and molybdate solutions added to the manure to obtain their final concentration in the manure solution mixture are presented in Appendix A.2. The computations in determining the volumes of

nitrite and molybdate solutions were obtained following the dilution formula $C_1V_1=C_2V_2$, where C is the concentration and V is the volume of the initial (1) and final (2) solution mixtures. The various amounts of concentrated nitrite and molybdate solutions calculated to reach their final concentration in the manure are shown in Table 4.2.

Table 4.1. Levels of nitrite, molybdate and combined nitrite and molybdate applied to manure of different ages (final concentration in the manure).

Manure Age	Nitrite (mM)	Molybdate (mM)	Nitrite and Molybdate (mM)*
Fresh	0 (control), 2, 5, 10, 20, 40, 50, 60, 80	0 (control), 0.5, 1.0, 1.5, 2.0	0 (control), 20 and (0.5, 1.0, 2.0), 40 and (0.5, 1.0, 2.0), 60 and (0.5, 1.0, 2.0), 80 and (0.5, 1.0, 2.0), 100 and (0.5, 1.0, 2.0)
1-month	0 (control), 5, 10, 20, 40, 60, 80, 100, 120	0 (control), 0.5, 1.0, 1.5, 2.0, 2.5, 3.0	0 (control), 20 and (0.5, 1.0, 2.0), 40 and (0.5, 1.0, 2.0), 60 and (0.5, 1.0, 2.0), 80 and (0.5, 1.0, 2.0), 100 and (0.5, 1.0, 2.0)
3-month	0 (control), 5, 10, 20, 40, 60, 80, 100, 120	0 (control), 0.5, 1.0, 1.5, 2.0, 2.5, 3.0	0 (control), 20 and (0.5, 1.0, 2.0), 40 and (0.5, 1.0, 2.0), 60 and (0.5, 1.0, 2.0), 80 and (0.5, 1.0, 2.0), 100 and (0.5, 1.0, 2.0)
6-month	None	None	None

* Numbers outside and inside the brackets are the final concentrations of nitrite and molybdate, respectively.

Table 4.2. Volume and concentration of the chemical agent concentrated solution applied to manure and resulting final concentrations.

Final nitrite concentration in the manure (mM)	Volume of nitrite solution applied (mL)	Final molybdate concentration in the manure (mM)	Volume of molybdate solution applied (mL)
0 (control)	0	0 (control)	0
2	0.304 (200 mM*)	0.5 mM	0.435 (35 mM)
5	0.770 (200 mM)	1.0 mM	0.883 (35 mM)
10	1.579 (200 mM)	1.5 mM	1.344 (35 mM)
20	0.435 (1400 mM)	2.0 mM	1.819 (35 mM)
40	0.883 (1400 mM)	2.5 mM	
50	1.112 (1400 mM)	3.0 mM	
60	1.344 (1400 mM)		
80	1.819 (1400 mM)		
100			
120			

* Numbers in brackets are the concentrations of nitrite and molybdate solutions added to manure

The addition of nitrite and molybdate to the manure was done separately and in combination. In the separate addition, nitrite or molybdate alone was added to the manure. For the combined addition of nitrite and molybdate, two different approaches were followed: 1) simultaneous addition of nitrite and molybdate, and 2) initial addition of nitrite and subsequent addition of molybdate. The sequential addition of nitrite and molybdate was performed based on the observation in the preliminary experiments in which nitrite reduced H_2S concentrations to very low levels but only for a short period of time following which H_2S concentration increased, while molybdate decreased H_2S to a low level and maintained it at that low level for a longer period. The sequential addition of molybdate was done approximately 24 hours after the initial application of nitrite, when H_2S concentration in the bottles has decreased to a low level. The combined addition of nitrite and molybdate was investigated with fresh and 3-month old manures only. Fresh and the oldest manure were only used since they represented the highest and lowest level of H_2S emissions. Six month old manure was not used as it was found during the experiment with individual addition of nitrite and molybdate that negligible level of H_2S was generated and emitted from the 6-month old manure. In another set of tests, nitrite and molybdate were added at the beginning of the test without waiting for H_2S concentrations in the headspace gas to reach a stable level. These tests were conducted to see the response in H_2S emission when treatment agents were added before accumulation of a significant level of H_2S.

4.1.2. Experimental setup

The laboratory-scale experiments were conducted in 125 mL serum bottles (Figure 4.1). The amount of manure added to each bottle was sufficient to produce an appreciable level of H_2S in the headspace gas, as reported previously (Predicala et al., 2008). Before the application of any treatment, the concentration of H_2S in the headspace gas in each bottle was monitored on a daily basis until it reached a stable level. Stability was assumed when variation of H_2S concentration in the headspace gas was around 100 ppm or less over three consecutive days. Once a stable level of H_2S was reached, specified amount of nitrite and/or molybdate were injected into the bottles. The immediate effect of nitrite and molybdate addition was determined by analyzing the headspace gas samples approximately 10 minutes and 2 hours after application of the reagents. Thereafter, sampling was carried out at longer intervals. Frequency of sampling was higher during the first 5 days (daily) and decreased gradually as experiments progressed (2-4 day intervals). After a period of 30-35 days sampling was performed once a month for a period of six months to assess the persistence of the treatments.

Headspace gas samples were analyzed using a gas chromatograph (GC) as described in section 4.4. Prior to sampling, each serum bottle was shaken by hand vigorously for approximately 10 seconds. Using a gas tight syringe, 30 μL of the headspace gas was taken from the bottle of which 20 μL was injected into the GC. To assess the reproducibility of the data and associated errors, experiments were carried out in duplicate. The bottles were kept inside a closed opaque container at room temperature (25 °C). At the end of the monitoring period, both treated and untreated (control) manure samples were sent for analysis of various properties to an external laboratory (ALS

Laboratory, Saskatoon, Canada). Another set of treated and untreated manure samples were also sent for determination of population of sulphate reducing bacteria (SRB) to another laboratory (PBR Labs Inc., Edmonton, Canada). For comparison, samples of fresh manure treated with 2.0 mM molybdate and 80 mM nitrite and 3-month old manure treated with 1.0 mM molybdate and 80 mM nitrite along with the untreated samples were sent for SRB analysis.

Figure 4.1. Serum bottles containing swine manure, sealed with rubber stopper and aluminium cap.

4.2. Semi-pilot scale tests in open top containers

The laboratory-scale experiments in closed systems were valuable in proving the effectiveness of the treatment and in exploring the impact of various influencing parameters such as manure age and the dependency of the required level of chemical agents on manure age under controlled conditions. However, the findings from these tests showed that the levels of H_2S in the headspace gas in closed systems were much higher than those which might be expected in an open system such as in typical swine

production rooms. Furthermore, positive results from these closed system tests with much higher H_2S levels indicate that the treatment could be equally effective when applied in actual barn conditions with much lower levels of H_2S emissions. Relying solely on the results from the closed system tests, however, could potentially lead to overestimation of the required level of the treatment reagents, thus a number of experiments were conducted in semi-pilot scale with open top containers in order to simulate practical conditions and to determine the realistic level of the reagent required for room scale application. Fresh manure was used in these open system trials because in the previous laboratory tests, the highest level of H_2S emission was observed with fresh manure. Furthermore, in a typical swine barn, large quantities of fresh manure are generated on a continuous basis, which serve as the main source of the H_2S and odour emissions. The results of laboratory scale tests also revealed that nitrite was effective in reducing H_2S levels but the impact was not persistent, while molybdate was effective in maintaining H_2S emissions at low levels over a prolonged period. Thus, only molybdate was used in these open system trials.

The semi-pilot scale tests were conducted in 6 open top cylindrical containers with approximate height of 60 cm and diameter of 186 cm. Manure was collected from the pit of a grow-finish room at PSCI using a submersible pump (Model WS-BHS, Goulds Pumps, ITT Corp., New York, USA). To ensure uniformity of properties of the manure samples, the pump was attached to a manifold system with six outlet pipes that allowed simultaneous loading of manure into six 75-L buckets. The buckets of manure samples were then transferred into the 6 open top containers in a nearby room, and the process repeated until each container is filled with approximately 250 L of manure. The

collected manure samples were left undisturbed overnight, then the calculated amounts of concentrated solutions of molybdate were added to containers to obtain molybdate final concentrations of 0.05, 0.1, 0.25, 0.5, and 1.0 mM. One container was designated as the control and did not receive any molybdate. Lower concentrations of molybdate (0.05 and 0.25 mM) were tested to assess their effectiveness and potential for decreasing the cost associated with the treatment. The concentrated molybdate solution was sprayed on the surface of the manure using a conventional hand pump sprayer. During the application manure slurry was gently agitated with a portable mixer to incorporate the reagent into the slurry. The open top containers were kept inside a ventilated and heated room in the PSCI research facility. Temperature of manure samples ranged from 15 to 20 °C throughout the experiment.

Sampling for H_2S emissions were done on the 10th, 20th, and 30^{th} day following the addition of molybdate. Using polyethylene tubes (approximate ID: 0.4 cm) as sampling lines, gas samples were collected from 5 locations within each container as shown in Figure 4.2. The inlet to each sampling line was placed approximately 5 cm above the manure slurry surface, as suggested by Jacobson et al (1997). One sample was collected from the centre of the tub, while the gas collected from the other four sampling ports located peripherally (10 cm from the tub sidewall) at equal distance from each other were combined as a single sample (composite sample). The headspace gas samples were collected into 1-L Tedlar bags with a septum-embedded cap (SKC Inc., Eighty Four, PA, USA) using a gas sampling set-up as shown in Figure 4.3 (Predicala et al., 2008). The setup, which operated based on the lung principle, consisted of a plastic container with a transparent lid fitted with ports controlled by 3-way valves. After attaching up to four

Tedlar sample bags in the sampling container, a vacuum pump used to evacuate the air from the container and to create negative pressure on the Tedlar bags, thus drawing in the gas sample from the sampling line attached to each bag. Prior to sampling, the Tedlar bags and sampling lines were flushed with nitrogen.

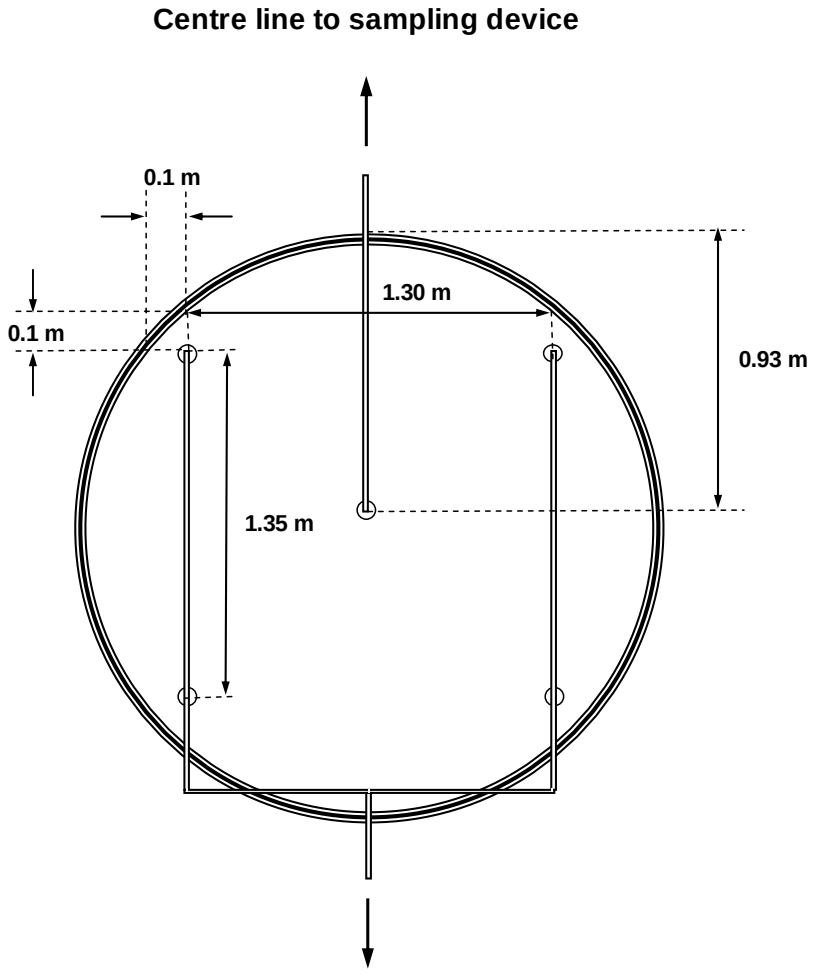

Figure 4.2. Top view of an open top container with sampling lines (small circles represent the location of sampling ports, with inlet opening at approximately 5 cm above the manure surface).

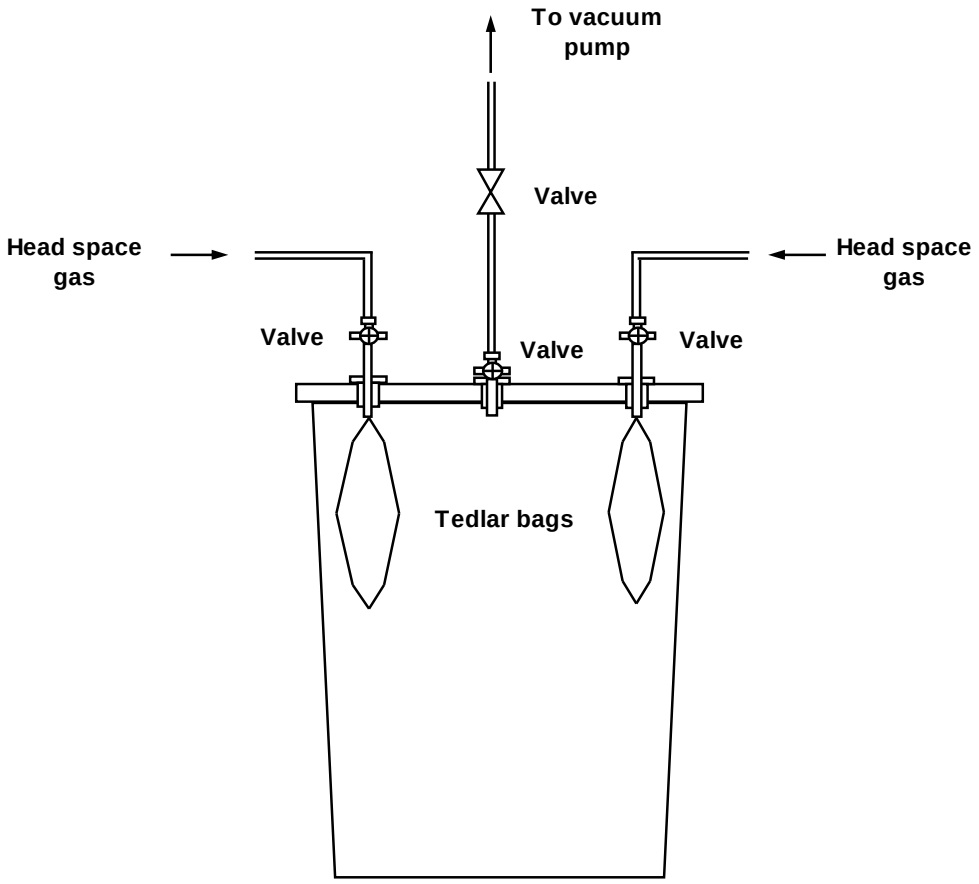

Figure 4.3. Schematic diagram of the set-up used to collect the gas samples in the open tub and room scale experiments.

To simulate conditions in actual swine production rooms, manure in the open top containers was agitated using the submersible pump. Gas samples were collected 2 minutes after the start of agitation. Duplicate bags from each sampling line (one from centre and one from peripheral composite line) were filled within 10 seconds. The bags were then transferred to the laboratory for analysis of H_2S with the gas chromatograph. Using a gas tight syringe, approximately 30 µL of the gas sample was removed from each bag of which 20 µL was injected into the gas chromatograph to determine its H_2S

content. This procedure was repeated at least twice and the average value of the readings was used.

4.3. Room scale tests

4.3.1. Room specifications

Upon completion of semi-pilot scale trials, effectiveness of molybdate addition in reducing H_2S emissions from swine manure was evaluated in room scale tests conducted in a setup similar to a commercial grow-finish pig production facility. This set-up included two identical and fully controlled environmental chambers located at the PSCI facility. Each chamber has inside dimensions of 4.2 m (L) × 3.6 m (W) × 2.7 m (H), with internal walls and ceiling covered with stainless steel sheets to eliminate emissions from these surfaces. Each chamber housed a pen for keeping 8 pigs throughout the experiment. The chambers and an adjacent room with the control equipment and instrumentation systems were enclosed in a big space ventilated with a centrifugal fan (Delhi BIDI-20, Delhi Industries Inc., Delhi, ON, Canada) that drew in fresh air through ceiling inlets. A 10-kW electric heater (Chromalox, Dimplex North America Ltd., Cambridge, ON, Canada) and a 5-ton air conditioning unit (Raka-060 CAZ, Setra Systems, Boxborough, MA, USA) were used to maintain the thermal condition of the air at the desired settings. The pre-conditioned room air was passed through a filtration unit (Circul-Aire USA-H204-B, Dectron International, Roswell, GA, USA) to remove particulates. The filtered air was split through a T-connection to supply air into the two chambers through an actuated air inlet located at the ceiling of each chamber. A 2-kW in-duct heater (Thermolec, Montréal, Canada) was located in the supply duct of each chamber to heat

the air when necessary. Additionally, each chamber had a negative-pressure exhaust fan (H18, Del-Air Systems Inc., Humboldt, SK, Canada) to draw the air out of the chamber into an exhaust duct leading to outside the building. The ventilation rate in each chamber was monitored using an iris damper (Continental Fan Manufacturing, Buffalo, N.Y., USA, accuracy ±5%) in the exhaust duct from each chamber. A Rapid controller system (Del-Air Systems Inc., Humboldt, SK, Canada) controlled the in-duct heaters, and the chamber inlets and exhaust fans.

Each chamber was configured to represent a conventional production pen, with slatted concrete floor on the front end and a solid floor extending towards the other end (Figure 4.4). The solid floor had a slope of 8% towards the slatted part. A commercial feeder was placed on one side of the penning of the solid floor and a cup-type water drinker was installed on the side of the slatted area to encourage the pigs to use this area for defecation and urination. A collection tub was placed under the slatted area to collect the mixture of feces and urine deposited on the slats. When necessary, manure deposited on the solid area was scraped towards the slats. The collection tubs in both chambers were identical in size (width:1.25 m, length: 2 m) and had a capacity of approximately 900 L.

4.3.2. Experimental procedures

Test duration and implementation: Trials were conducted in both chambers simultaneously, with one chamber used as the control and in the other treatment was applied. Before initiating the experiment, both chambers were pressure-washed, cleaned and disinfected. The ventilation controller sensors and air quality monitoring instruments

were tested and calibrated. Eight female pigs with a starting average weight of about 30 kg were placed in each chamber. Overall, three trials were performed with the first trial used as a preliminary run to anticipate the levels of H_2S that can be generated from the rooms as well as establish various procedures and monitoring protocols. The established protocols were then applied in the subsequent trials which were conducted over a period of 48 days.

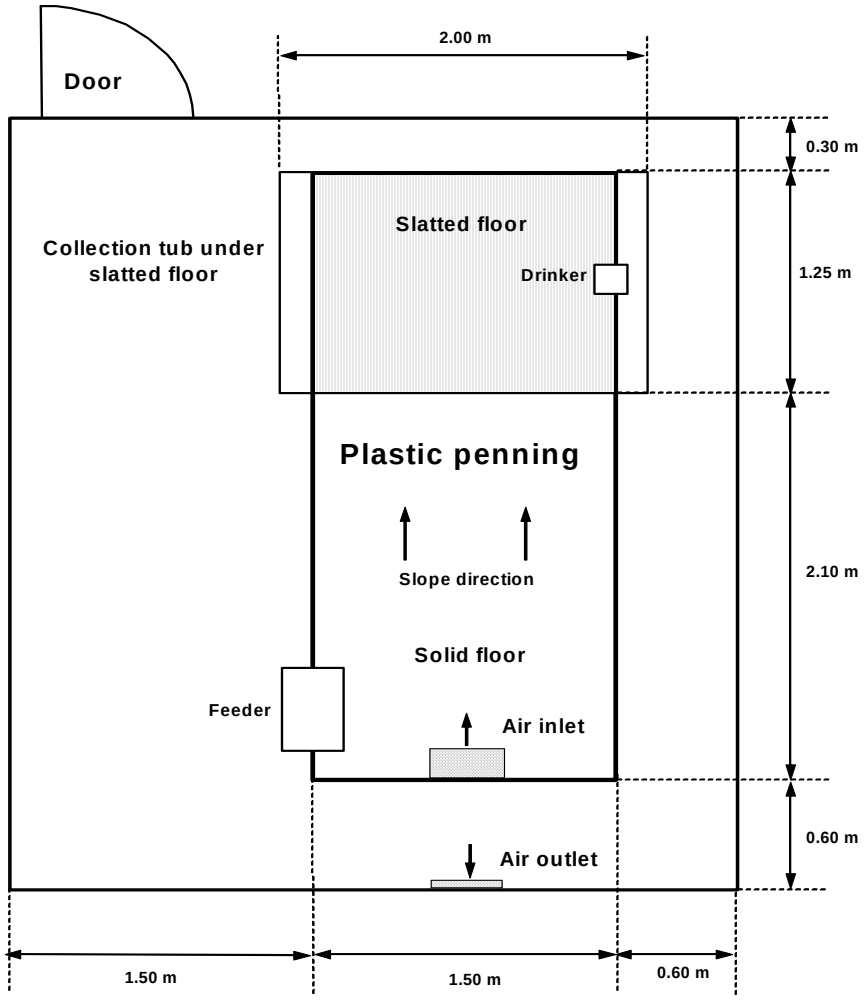

Figure 4.4. Lay out of an environmental chamber used for room scale experiments.

At the start of the trials, the pigs were trained to use the slatted area for urination and defecation and the solid floor area as laying area. This was achieved by wetting the slatted area with water and keeping the solid area dry by regular scraping of any feces and urine deposited on the solid floor. Pigs were fed standard barley-based grow-finish diets formulated to meet nutrient requirements for growing pigs (NRC, 1998). The standard diet used in the current study contained approximately 55 - 65% barley, 15-25% peas, 5-15% wheat, oats and soybean meal, and vitamins and minerals (NRC, 1998). Diets were reformulated based on the growth stage of the pigs. Therefore, relative amounts of grains changed during the trials (4 different diets were used in total).

Daily health checks were conducted. Following the standard temperature guidelines for grow-finish pigs, temperature in the chambers was initially set at 21ºC and gradually decreased to 16ºC by the last week of the trial (PSCI, 2000).

The first 18 days of the trial served as manure accumulation period. On day 18, a concentrated solution of molybdate (10 mM) was applied using a portable pump sprayer to the manure slurry in the collection tub of one of the chambers (Treatment) to achieve a final concentration of 0.1 mM. This concentration was chosen based on the results of the open top container tests in which 0.25-0.5 mM molybdate was sufficient to control the emission of H_2S and from preliminary tests in the room setting which revealed a much lower level of emitted H_2S when compared with open top containers. Molybdate solution was mixed with the manure by moving a rake over the entire length of the manure collection tub twice. In the other chamber (Control), water (same volume as that of the molybdate solution) was added to the manure following the same procedure used in the Treatment chamber. Preliminary trial results showed that the amount of manure produced

during the tests was higher than the capacity of the tubs, thus in subsequent trials, pre-determined amount of collected manure (212 L) was removed from the collection tubs immediately after the first and second sampling events to allow for sufficient room in the collection tubs for the manure produced between the two sampling events. The amount of manure removed was based on the average rate of manure production observed 10 days before the sampling date (e.g. after the first sampling, approximately 212 L were removed based on the average of 21.2 L/day of increase). Following the removal of manure from each chamber, additional concentrated molybdate solution (5 mM) was added to the tub in treatment chamber to compensate for decrease in concentration of molybdate due to removal of treated manure and accumulation of fresh manure between two sampling events.

Sampling and data collection: During the course of the experiment, regular monitoring of gas concentrations in both chambers, specifically H_2S, NH_3 and carbon dioxide (CO_2), as well as the air quality parameters (room air temperature, relative humidity, ventilation rates) were done. Manure production, water use and feed intake and weight gain of the animals were also monitored. The levels of H_2S emitted gas from the manure tubs were determined on days 28, 38 and 48. Concentrations of NH_3 and CO_2 were determined using gas analyzers with sampling points placed at the ventilation air inlet and outlet of each chamber. Over a 24-hour monitoring period, NH_3 and CO_2 concentrations were measured at 15 minute intervals once a week and also during and after each H_2S sampling event.

The air temperature and relative humidity in both chambers were measured every 5 minutes while the ventilation rate was recorded every 1 minute. Type T thermocouples

and portable humidity sensors (Model F22H, Rotronic Instrument Corp., Huntington, New York, USA) were installed to measure temperature and humidity, respectively. The measurements were logged and stored using a datalogger (Model CR1000, Campbell Scientific, Logan Utah, USA).

The manure production in each tub was monitored daily. The volume of the tubs was measured before the start of the experiment by gradually adding known volumes of water and then consequently measuring their respective depths. A relationship between the depth and volume of the water was then derived and an equation was developed. Manure volume in each tub at any time was calculated based on the measured depth using this equation. Manure production was then determined by the difference in volume at the end and start of the tests.

The water and feed consumption by the pigs were also monitored. Water usage in each room was measured daily. A water meter (Type SF, ABB Water Meters Inc. Florida, USA) attached to a drinker in each room was used to measure water usage. For the feed intake, all feed supplied to the animals were weighed and recorded. The average daily feed intake during the course of the tests was calculated per pig. The average daily gain of the animals was also determined based on the difference in weight of the animals at the end and beginning of the tests.

Gas sampling procedure: To determine the spatial H_2S distribution at specific locations of interest within the chamber, gas samples were collected at three elevations in the room. As shown in Figure 4.5, the locations were situated at the pit (approx. 5 cm above manure surface), and at animal- and human-occupied zones. Prior to the gas

sampling, pigs were moved to an adjacent room. To commence sampling, manure slurry in the tub was agitated using a submersible pump and a custom-made steel rake. This procedure was intended to simulate the actual practice in swine production barns wherein the manure collected in underfloor pits was periodically cleared out by draining by gravity flow through drain holes on the floor of the pit, thereby agitating the slurry. The agitator pump had two outlets, placed at the opposite corners of the tub, which discharged the slurry about 10 cm above the manure surface. This configuration ensured the flow of the manure in a swirling pattern, similar to the flow pattern of slurry during the drainage of manure pits in swine barns. To ensure the release of H_2S caused by complete agitation of all layers of slurry including the settled solids, a long-tined rake spanning the tub width was moved back and forth over the length of the tub simultaneous with the operation of the agitator pump. Agitation continued for 5 minutes, while gas samples were collected at 2 and 5 minutes after the start of agitation in the first sampling event, and 2, 5, 10 and 15 minutes in the second and third sampling events. At the pit level, six sampling ports were placed approximately 5 cm above the manure surface while one port was placed for each of the pig and human levels as outlined in Figure 4.5. The sampling tubes were connected to the gas collection set-up (Figure 4.2) and gas samples were transferred to the Tedlar bags following the procedures described earlier. The filled sample bags were then transferred to the laboratory for analysis. The pigs were returned to the room after sufficient ventilation of the room and removal of the emitted gases which was verified with portable H_2S gas monitors (Model Pac III, Draeger Safety Inc., Pittsburgh, PA; 1 ppm precision). . It should be pointed out that ventilation air entered the chamber through a ceiling inlet with a baffle which directed the incoming air toward the wall opposite the

exhaust fan. The size of inlet opening is controlled by an actuator attached to the baffle, the operation of which is integrated with the heating and ventilation controller system of the chamber. The inlet baffle induced a jet flow close to the ceiling which created a circulating air flow pattern within the room and prevented the short circuit of the air between inlet and outlet (Figure 4.4) Temperature, humidity, ventilation rate, manure production, water usage, average daily feed intake, and weight gain were also monitored.

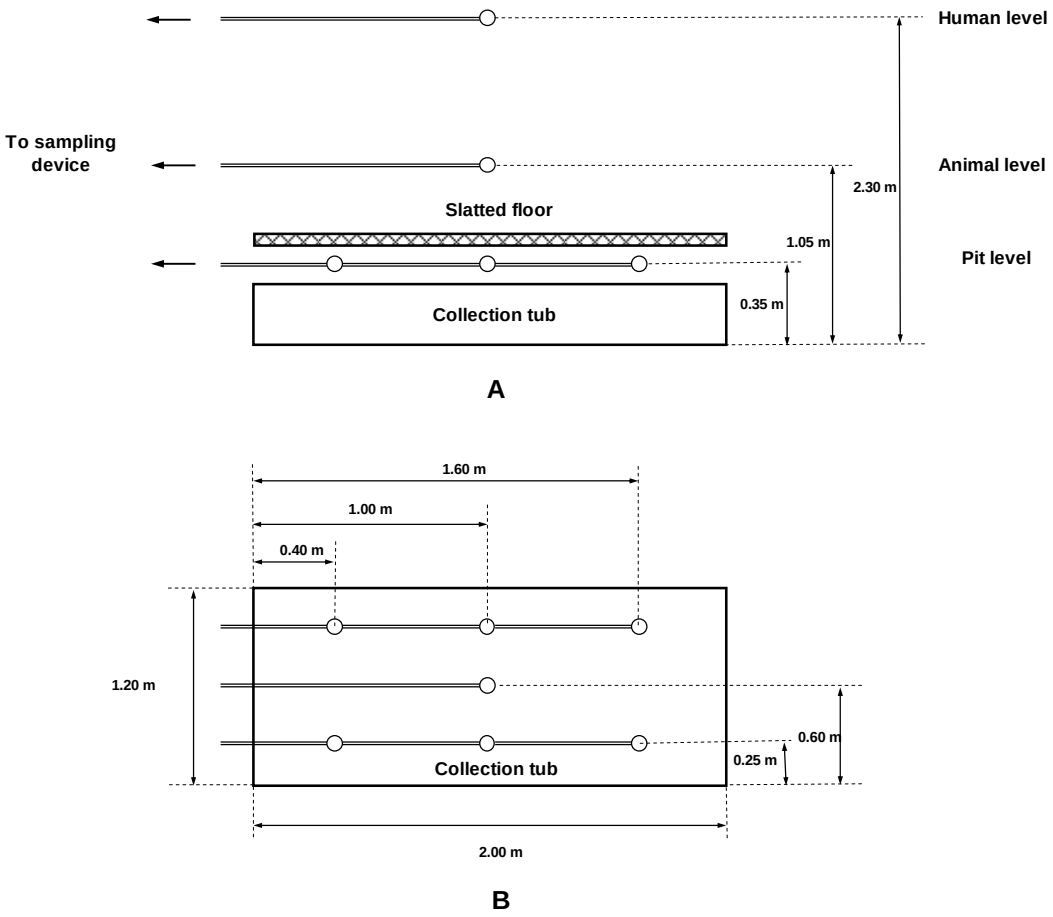

Figure 4.5. Schematic diagram of the gas sampling lines installed inside the chamber A: frontal view, B: top view.

4.4. Analytical procedures

The analysis of the gas samples for H_2S content was carried out with a Varian CP-3800 gas chromatograph (GC) equipped with pulsed flame photometric detector (PFPD). The GC was installed with a GS-GasPro 30 m × 0.32 mm I.D. capillary column (Agilent Technologies, Canada). The carrier gas was ultra high purity grade nitrogen at a flow rate of 2.0 mL/min. The column oven was maintained at 100 °C throughout each run. The chromatograph was calibrated using calibration gases containing 0.44, 1.24, 19.4, 98, 200, and 1954 ppm H_2S, balanced with nitrogen (Praxair, Saskatoon, Canada). Three calibration curves (quadratic with R^2 values greater than 99%) were generated covering different concentration ranges of 0.44-19.4, 19.4-200, and 98-1954 ppm H_2S. Each point of the calibration curve represented the average value of at least four measurements. The GC injector was operated at 200 °C and split ratios of 1:8, 1:25, and 1:60 were used for the low, medium and high concentrations range, respectively. Each collected sample was injected at least twice to verify the reproducibility of the results. Furthermore, a calibration gas sample was injected after every 30 samples to ensure the accuracy of the results and to check for drift. GC was recalibrated if the error in the measured concentration of the calibration gas was more than 10%.

Ammonia and carbon dioxide concentrations were determined by an ammonia analyzer (Model Chillgard RT, MSA Canada, Edmonton, AB; accuracy of ±2 ppm) and a carbon dioxide analyzer (Model Guardian Plus, Topac, Hingham, MA; accuracy of ±60 ppm), respectively. Both analyzers were calibrated using zero and span gases prior to their use in the experiment. A programmable logic controller (PLC) system was used to

facilitate distribution of gas samples through polyethylene tubes from the chambers to a sampling manifold and then into the analyzers.

4.5. Soil test

4.5.1. Description of soil plot

A field previously planted with wheat was selected for the soil tests. Three plots were made each with dimensions of 0.5 m x 0.5 m. The plots were arranged side by side. The position of the plots was configured in a way that the overall length of the plots was perpendicular to the direction of the field gradient. A shed was constructed to shield the plots and to prevent interference by rain events. The shed was assembled with slatted walls and roof covered with transparent polyethylene sheets to allow sunlight to reach the plots. Each plot was installed with a polyethylene sheet around its perimeter up to a depth of 45 cm to prevent water or manure from seeping into or out of the plot.

4.5.2. Experimental procedures

The manure samples used for the soil test were collected from the environmental chambers (control and treated) right after completion of the room test (the last H_2S sampling event). It was important to collect the samples immediately after agitation to obtain a homogenous representative sample. A 2-L sample was collected from the center of the tub in each chamber and transferred into clean plastic containers. After collection, the containers were placed inside a freezer and the samples were frozen at -20 °C until they were used for the soil test.

One plot was applied with manure from the control chamber, the other with the manure from the treated chamber and the third plot was used as a control without any

added manure. Prior to the application of manure, water was added to all the plots to field capacity to normalize the soil conditions between the plots. To attain field capacity in the plots, 8 L of tap water was slowly poured into each plot to saturation. The plots were then left undisturbed for 2 days which allowed drainage of the excess water and achieving field capacity (Wang et al., 2001). After the soil had attained field capacity, manure was added to the selected plots. The amount of manure added to each plot was based on the recommended agronomic rate of 37,000 L/ha which is equivalent to about 100 kgN/ha (Lipoth and Schoenau, 2007; Stumborg et al., 2007; Stumborg and Schoenau, 2008). This rate is equivalent to 925 mL per plot.

In preparing the manure for application, the frozen manure was thawed overnight inside a refrigerator (4 °C). Immediately before application, the manure was thoroughly mixed and 925 mL was set aside for application. The rest of the manure sample was sent for analysis of various properties. The application of manure to the plots was done by broadcasting in a grid system. Each plot was divided into a grid of 50 sub-plots of 0.1 m x 0.05 m in size. Based on the required agronomic application rate and the area of each sub-plot, 18.5 mL of manure was measured using a 200-mL graduated cylinder and then carefully poured into each sub-plot so as to contain the manure within the specified area. The same procedure was repeated until all 50 sub-plots were filled.

After manure application, the plots were left undisturbed for 1 week. This period was allotted to sufficiently allow the manure to equilibrate and fully integrate with the soil. After 1 week, soil cores were collected from each plot. Soil core samplers, made from PVC pipe with diameter of 15 cm and height of approximately 35 cm, were used to collect the soil core samples. One core was taken from the center of the plot and another

near the edge. Uniform soil core sizes (15 cm diameter x 30 cm) representing soil profile down to 30-cm depth were collected. Each core was then divided into three sections, with the 0-10 cm depth as the top section, 10-20 cm depth as middle section, and the 20-30 depth the bottom section. Each section was placed inside a clean polyethylene bag. The soil samples were roughly ground by hand. To dry the samples, the bags were left open and set aside for 1 week at room temperature. Following this, a composite sample of each section from each plot which consisted of the samples taken from the centre and edge of the plot, was prepared and sent for analysis (ALS Laboratory, Saskatoon, Canada). Each composite sample was analyzed for available N, P, K, salinity, molybdenum content, total coliforms, aerobic/heterotrophic bacteria population and pH. Along with these tests, manure samples of the same batch used in the test, were also sent for analysis of properties similar to the test done for the serum bottle samples.

4.6. Statistical procedures

In the semi-pilot and room scale tests, the effectiveness of treatments with respect to the control was analyzed by repeated measures, over the successive sampling events, using the SAS version 9.1 software (SAS Institute, Inc, NC, USA). The effect of independent variables (treatments) and their interactions on the dependent variable (H_2S concentration) was tested using the SAS Mixed procedure with α=0.05. Following the determination of significant differences between means, comparison of means was carried out using a post-hoc method, specifically Tukey-Kramer. The selection of the method was based on its ability to minimize the probability of getting a family-wise type I error (Mendenhall and Sincich, 2007). Prior to conducting repeated measures analysis,

the normality of data was tested using the Univariate procedure in SAS. In cases where the initial normality check showed non-normal distribution of data, a log-transformation of the data was done. After confirmation of normality, the log-transformed data was analyzed for repeated measures.

5. RESULTS AND DISCUSSION

5.1. Laboratory scale tests

After the manure samples of desired age were prepared, filled into serum bottles and sealed as described in Section 4.1, the headspace gas of the serum bottles was monitored closely until a stable level of H_2S was attained prior to the application of nitrite and/or molybdate treatments. During the first 7 days after filling the serum bottles, H_2S concentration initially increased up to a certain level, and then fluctuated around that level afterwards. A stable H_2S level was assumed to be attained when variation in H_2S concentration over three consecutive days was around 100 ppm or less. Regardless of manure age, stable level was achieved 1-2 weeks after the manure sample was sealed in the serum bottles.

5.1.1. Effect of manure age

To evaluate the effect of manure age on H_2S concentrations, the profiles of H_2S concentrations in the untreated (control) systems containing fresh, 1-month and 3-month old manures are shown in Figure 5.1. For fresh manure, the concentration of H_2S in the headspace gas became stable at around 4792 ppm, then increased slightly to 5771 ppm after 4 days, after which gradually decreased to 4773 ppm at the end of the monitoring period (25 days).

The average concentration of H_2S in the control system (with fresh manure) throughout the test period was 4856±460 ppm. The same trend was observed in the control systems with 1-month and 3-month old manures having average H_2S concentration of 3431±208 and 1037±98 ppm, respectively. With 6-month old manure, a

set of 15 bottles were filled and monitored for H_2S. The concentrations measured in the headspace gas from all the bottles were below the detection limit (<0.4 ppm), even after 2 weeks of constant monitoring. Hence, we did not proceed with the tests on treatment of 6-month old manure with nitrite or molybdate.

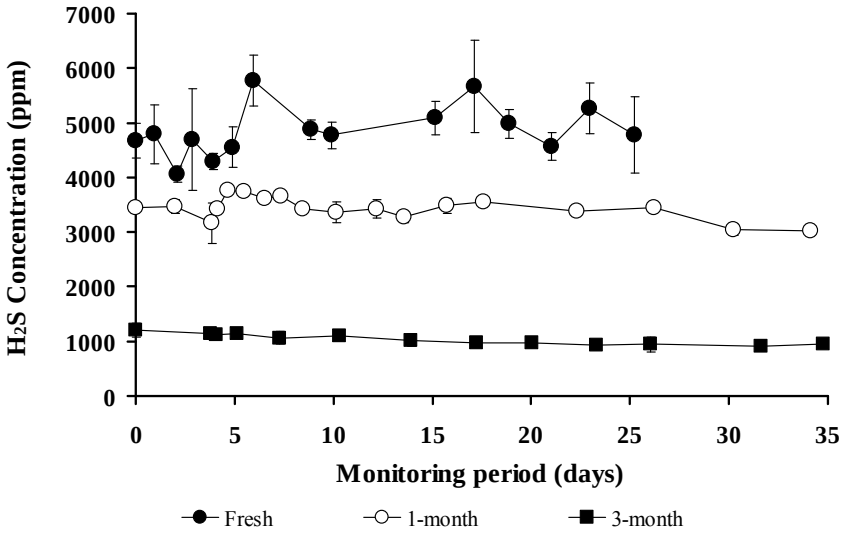

Figure 5.1. Profiles of H_2S concentration in the headspace gas of untreated (control) systems with fresh, 1-month and 3-month old manures.

The findings presented above show that the level of emitted H_2S decreased as the manure age increased. Fresh untreated manure had the highest concentration of H_2S emitted while 6-month old manure produced relatively undetectable levels of H_2S. This observation indicates that storage time of manure affects the level of emitted H_2S. The decrease in H_2S level in the headspace gas of serum bottles over time could be due to two mechanisms: 1-spontaneous oxidation of H_2S gas inside the closed system, 2- inhibition of SRB present in the manure thereby preventing the production of more H_2S. Clanton and Schmidt (2000) found that concentrations of H_2S as well as dimethyl sulphide and

carbon disulphide, emitted from swine and dairy manure, were affected with time. Air carbon disulphide decreased at a rate of about 1 ppb/day while the total reduced sulphur decreased by 0.03 ppb/day during the end of the study. A previous study also showed that H_2S levels from swine manure were changed over a three-week period (Avery et al., 1975). Hobbs et al. (1999) studied the production and emission of odours and gases emitted from ageing swine manure and found that the emission rate of H_2S decreased from 100 to 28 g/m^2d over a storage period of 112 days. They observed that the production of H_2S from manure increases during the initial portion of the storage period and decreases once it reaches a maximum. Arogo et al. (2000) found that concentration of H_2S was highest during the first five to ten days of introduction of swine manure into a storage pit. This finding conforms to the behaviour of H_2S in the serum bottles wherein the concentration initially increased and then reached stabilization after 1-2 weeks.

5.1.2. Effect of separate of addition nitrite and molybdate to manure of various ages

The profiles of H_2S concentration in the headspace gas of serum bottles containing fresh manure treated with various amounts of nitrite or molybdate are shown in Figure 5.2. Each data point in the figure is the average value of H_2S concentrations observed in the duplicate tests (two samples from each set, n=4) and the error bar is the associated standard deviation. The error bar is not visible for some data points as the associated standard deviation is small. The average value for the standard deviations calculated for the entire laboratory test results was 61 ppm, indicating reasonably reproducible results. The same trends in the profiles of H_2S concentration shown in the figure were also observed with 1-month and 3-month old manures. A summary of these

observations is presented in Figure 5.3. The complete set of H_2S concentration profiles for 1-month and 3-month old manures are presented in Appendix Figures B.1 and B.2 respectively.

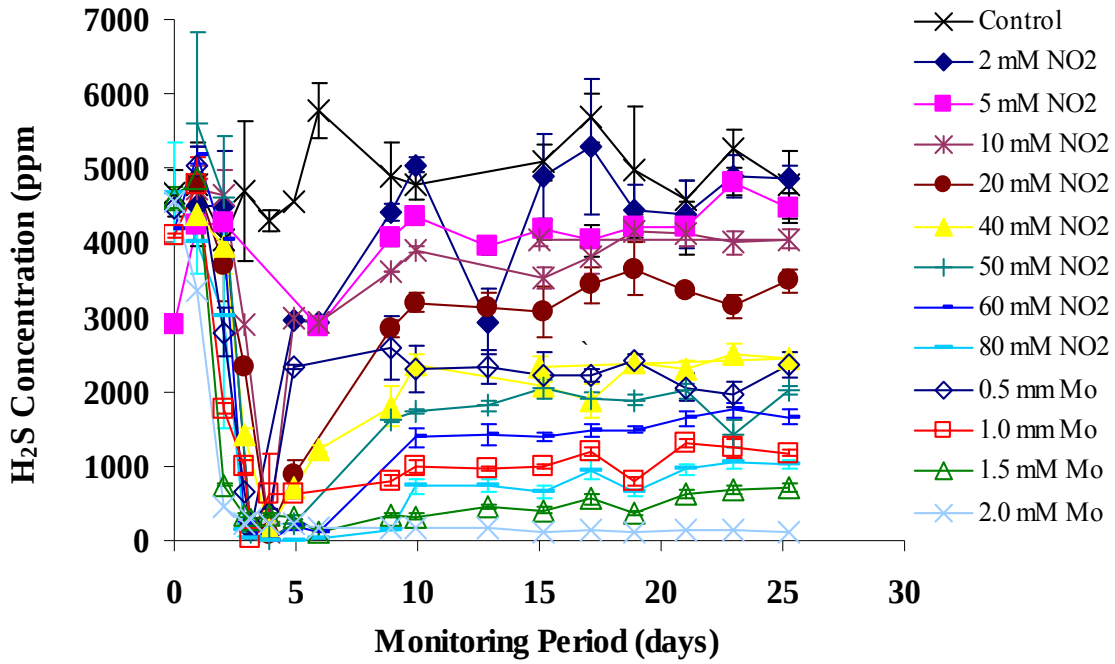

Figure 5.2. Profiles of H_2S concentration in the headspace gas of serum bottles containing fresh manure treated with various amounts of nitrite and molybdate.

Figure 5.3 shows the profiles of H_2S concentration in the headspace gas of serum bottles containing fresh, 1-month and 3-month old manures treated with varying quantities of nitrite (2-120 mM) and molybdate (0.5-2 mM). For reference, the H_2S profiles for the untreated (control) systems were also included. To avoid congestion of data, only a representative number of tested conditions are shown in these figures. As can be observed from the plots, the decreasing levels of H_2S with increasing manure age led to lower levels of nitrite and molybdate required to reduce its emissions.

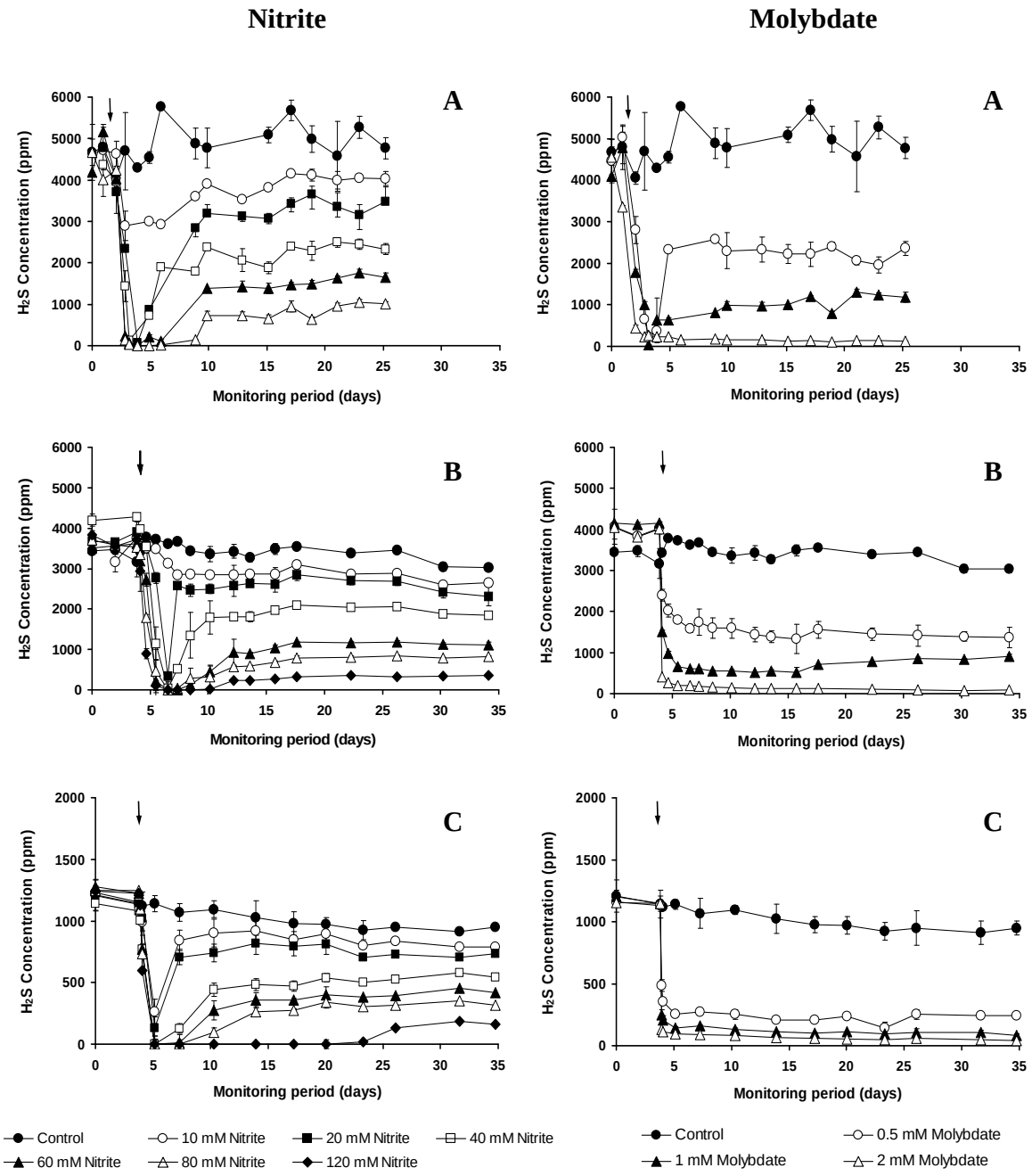

Figure 5.3. Profiles of H_2S concentration in the headspace gas of the serum bottles containing fresh (A), 1-month old (B), and 3-month old (C) manures treated with nitrite or molybdate separately. Arrows indicate the addition of the chemical. (The highest concentration of nitrite applied to fresh manure was 80 mM).

Nitrite treatments

Regardless of manure age, the addition of nitrite, especially at higher concentrations, sharply decreased the concentration of H_2S over a period of 24-36h to a low level. After this period, sulphide concentration increased and stabilized at values which were dependent on the level of applied nitrite and the manure age. With fresh manure the lowest level of H_2S (<10 ppm) was only observed when 80 mM nitrite was applied. With 1- and 3-month old manures, the same level of H_2S was observed when nitrite concentrations of at least 60 and 40 mM, where applied, respectively.

The addition of nitrite did not keep the concentrations of H_2S at the low level and H_2S concentration in all nitrite treated conditions gradually increased and eventually levelled off. For instance, with 80 mM nitrite added to fresh manure, H_2S concentration increased to 1018 ppm after 25 days of monitoring. Even at five months after application, the level of H_2S was maintained around 1012 ppm. In the untreated system the concentration of H_2S decreased from 4773 to 2050 ppm over a period of 5 months.

The same trend was observed with 1-month old manure where the concentration of H_2S six months after the addition of 120 mM nitrite (highest amount for nitrite treatments) slightly increased to 435 ppm from 366 ppm at day 30 despite the decrease of H_2S level in the control bottle to 1130 ppm. With 3-month old manure, the addition of 120 mM nitrite slightly reduced H_2S concentration from 159 ppm at day 30 to 140 ppm after 6 months; however, a similar decrease in H_2S level in the control from 948 to 640 ppm was observed.

Although the addition of nitrite did not maintain a low level of H_2S, the final concentrations in all tested cases were below the level observed in the control system,

even after the extended period of six months. The final concentration of H_2S at the end of the 30 day monitoring period was also dependent on the level of applied nitrite and manure age (Fig. 4.4a). The concentration of H_2S was lower as higher levels of nitrite were applied and as manure age increased. For instance, the final concentrations of H_2S following the treatment with 20 and 80 mM nitrite were 3415±182 and 818±166, 2576±149 and 763±90 and 749±46 and 310±32 ppm, in the fresh, 1-month and 3-month old manure, respectively. In all cases, final H_2S concentration was lower than that in the control system and the observed difference was statistically significant ($P<0.05$; pair t-test, Excel Software, Microsoft Corporation). These values were the average of the concentrations observed from the time H_2S leveled off until the end of experiments (Day 10-35). The lowest final H_2S concentration with nitrite treatments (159±28 ppm) was achieved when 120 mM nitrite was applied to 3-month old manure.

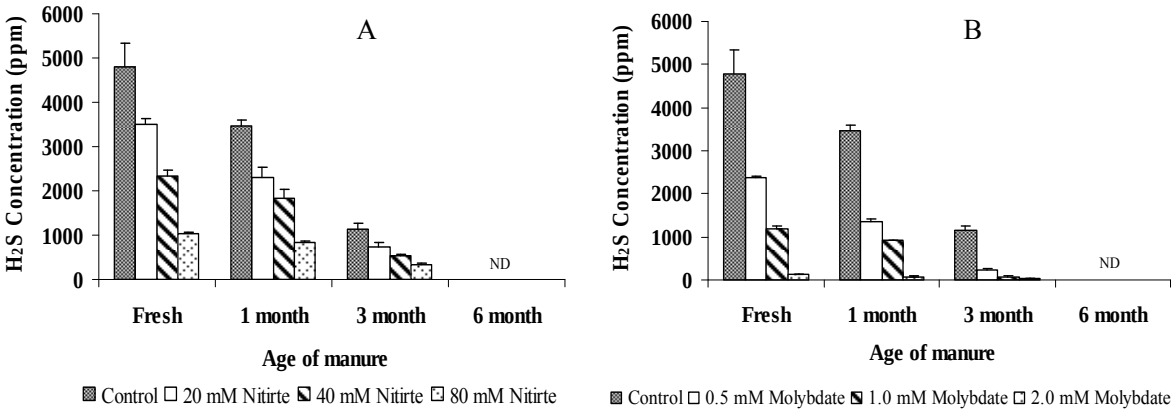

Figure 5.4. Average final concentration of H_2S at the end of monitoring period in the headspace gas of the serum bottles containing swine manure of different ages treated with nitrite (a) and molybdate (b). (ND: not detected)

Molybdate treatments

The effect of manure age on the required level of molybdate for control of H_2S emissions was similar to that of nitrite. Since H_2S concentrations were lower with increasing manure age, the level of molybdate required to reduce these concentrations were also lower. As with the effect of nitrite addition, the application of molybdate caused a sharp decrease in the concentration of H_2S regardless of manure age. However, unlike nitrite in which H_2S concentration abruptly increased after a short period, the low level of H_2S after molybdate addition was maintained or decreased further during the remaining period of the experiment (Figure 5.3, right panels). The only exception was the case where 0.5 mM molybdate was added to fresh manure in which H_2S concentration increased from a residual value of 222 ppm to values as high as 2584 ppm during the remaining period of monitoring. This behaviour was considerably similar to the profile of H_2S concentrations when 40 mM nitrite was added to fresh manure (Figure 5.3 A).

Similar to the response observed with nitrite, higher levels of molybdate and increases in manure age both led to lower levels of residual H_2S (Fig. 5.4b). After 30 days of monitoring, the final concentrations of H_2S following the treatment with 0.5 and 2 mM molybdate were 2278±176 and 142±22, 1452±97 and 105±19, and 231±37 and 51±7 ppm, for fresh, 1-month and 3-month old manure, respectively. The lowest level of H_2S was 42±5 ppm achieved when 3-month old manure was treated with the highest level of molybdate (3 mM).

Monitoring of the bottles treated with molybdate over a period of six months confirmed the persistency of the molybdate treatment. After this extended period, the concentration of H_2S was either maintained at the observed level following the treatment

or further decreased. For instance, the level of H_2S in the fresh manure treated with 0.5 and 2 mM molybdate was further reduced to 1122 ppm and 73 ppm, from 2360 ppm and 124 ppm respectively. With 3-month old manure, the decrease was more pronounced with H_2S levels decreased to 116 and 9 ppm with the addition of 0.5 and 2 mM molybdate, respectively.

Although the effect of molybdate was found to be persistent, it did not reduce H_2S concentration to the low levels which were temporarily observed when nitrite was used. For instance addition of nitrite temporarily reduced the residual levels of H_2S below the detection limit (0.4 ppm) when applied to 1-month and 3-month old manures, especially with high doses of nitrite (>60 mM). It should be reiterated that this substantial reduction in H_2S concentration was only temporary and H_2S concentrations rose back and eventually leveled off. As for molybdate, once H_2S concentrations were reduced, they were generally maintained at the low level and in certain occasions further decreased. The persistence of molybdate makes it a more effective treatment option when compared to nitrite especially since swine facilities generally store manure for a considerable period of time.

One could attribute the variations in the level of emitted H_2S with manure age to the changes in the physical and chemical properties of the manure during storage. Another possibility is that the variation in biological conditions like the number and viability of the resident microbial population especially sulphate reducing bacteria, or the availability of sulphate, the precursor for formation of sulphide caused a lower level of H_2S emission with the aged manure. Table 5.1 summarizes the properties of untreated manure at different ages. It includes the properties of manure applied with 2, 1.5 and 1

mM molybdate, the most effective treatments found in each manure age category. As can be seen from the table, apart from the total organic carbon (TOC) and molybdate contents, the other properties of treated and untreated manure were similar. Furthermore, it seems that the storage of manure (increase in age) did not change the properties of the manure. This suggests that these properties may not be responsible for the change in the level of emitted H_2S at least with regards to the storage period. However, it should be noted that the test for properties was done with only one composite sample (from duplicate tests) for the treated and untreated system in each manure age. Additional tests should be conducted to verify these results. The higher level of TOC observed in the treated manures when compared with the untreated ones (regardless of age) could be due to inhibition of microbial activity by the added molybdate which in turn hampered the utilization of the biodegradable organic contents of the manure by the present microbial population.

Table 5.1. Properties of the fresh and aged manures before and after treatment with molybdate in the serum bottles (unless otherwise stated all the properties are in mg/kg dry manure).

Property	**Fresh manure**		**1-month old manure**		**3-month old manure**	
	Control	**2.0 mM Mo**	**Control**	**1.5 mM Mo**	**Control**	**1.0 mM Mo**
TOC	1900	3800	1600	3700	2100	2400
Ammonia	3100	2800	3100	2900	3000	2900
Kjeldahl N	3300	3000	3200	3100	3300	3200
Protein	20600	18800	20000	19400	20600	20000
P	265	222	241	221	268	242
K	2000	1850	2110	1890	2010	1870
S	124	171	99	155	112	107
Nitrite	0.65	0.85	0.72	0.7	0.66	0.79
Mo	<1	182	<1	165	<1	89.9
Total Solids (%)	0.9	1.2	0.9	1.2	0.9	1.0
pH	7.9	7.8	7.9	7.7	7.9	7.9

n=1

Additionally, the physical appearance of untreated fresh, 1-month and 3-month old manures were closely similar, while the 6-month old manure looked darker in colour and contained finer solids. A difference in colour was also observed between the manure in the untreated system and the ones applied with nitrite and molybdate. The manure in the untreated system was greyish black in colour while manure with added molybdate was distinctively brownish in colour. On the other hand, manure with applied nitrite appeared in a somewhat grey and yellow colour combination.

5.1.3. Combined addition of nitrite and molybdate

The results of the tests with the separate addition of nitrite and molybdate revealed that nitrite was able to reduce the H_2S content in the headspace gas to its lowest level (<0.4 ppm) within 36 hours after addition but on a temporary basis. It was also found that molybdate was not capable of reducing H_2S levels as low as that with nitrite but its effect was persistent and no increase in H_2S concentration was observed over an extended period of monitoring. Considering the individual capabilities of nitrite and molybdate, it was speculated that the addition of nitrite and molybdate in combination may decrease H_2S to significantly low levels which would be maintained over a prolonged period of time.

In these tests, only fresh and 3-month old manures were used since based on the effect of manure age, they represent the upper and lower limits of H_2S emission, respectively. The combined addition of nitrite and molybdate was applied either simultaneously or sequentially. In the sequential addition, nitrite was added first and following the decrease of the H_2S concentration to a low level molybdate was applied

(approximately 24 h. interval between these additions). The same levels of nitrite and molybdate (same combinations) were used in both the simultaneous and sequential addition tests.

Figure 5.5 shows the H_2S concentration profiles from fresh manure treated with various amounts of nitrite and molybdate added simultaneously (Panel A) or sequentially (Panel B). The complete set of H_2S profiles for all tested conditions in case of simultaneous and sequential addition of nitrite and molybdate to fresh manure is presented in Appendix Figure B.3 and B.4 respectively. As can be seen in the plots, there was no significant distinction between the effects of simultaneous and sequential addition of nitrite and molybdate.

Looking at the levels of emitted H_2S, the concentrations observed with combined nitrite and molybdate were similar to the levels measured during the test using fresh manure when nitrite and molybdate were added individually. As shown in Figure 5.5, although the level of H_2S in the untreated system was gradually decreasing towards the end of the experiment, the average concentration throughout the monitoring period was 4463±554 ppm which is relatively close to the average concentration of 4856±461 ppm observed in the control system in the previous tests with individual compounds. This finding would indicate that the H_2S production with fresh manure was consistent in these separate tests, thus comparison of the treatment results would be justified.

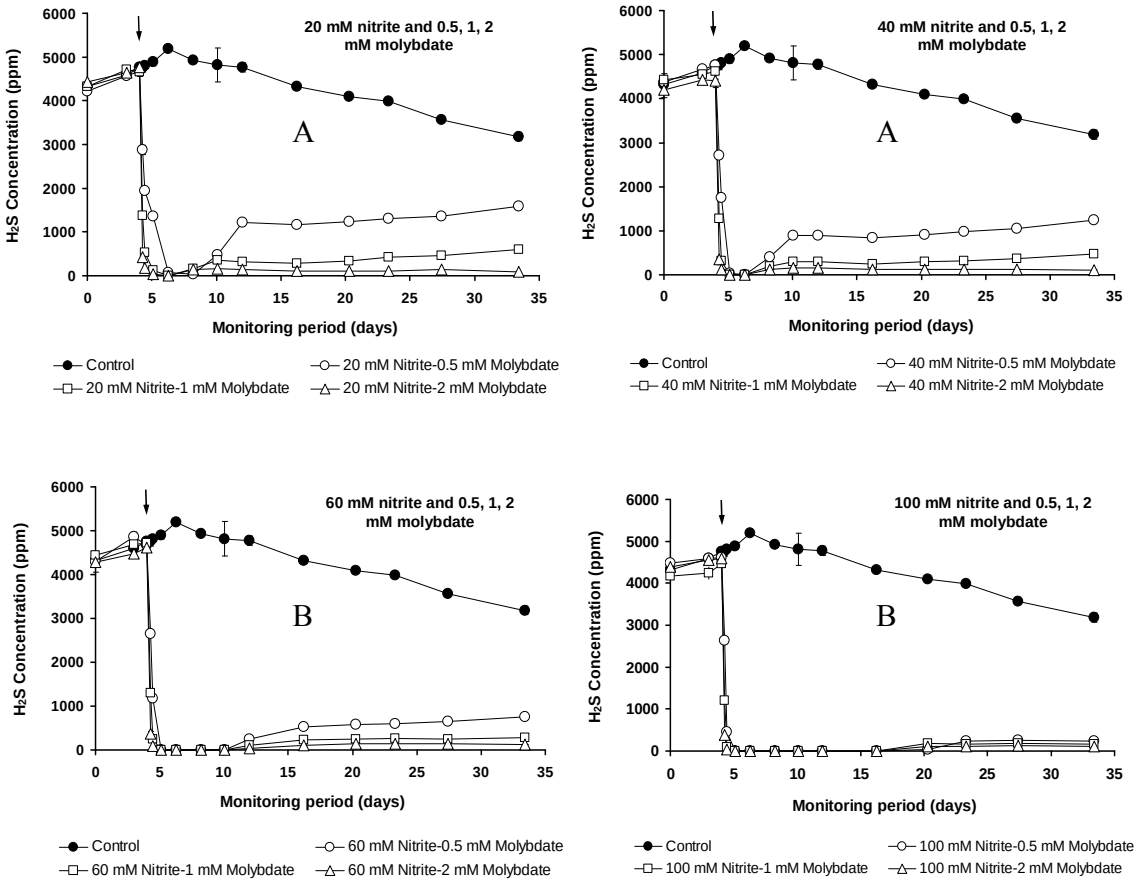

Figure 5.5. Profiles of H_2S concentration in the headspace gas of the serum bottles containing fresh manure treated with various amounts of nitrite and molybdate added simultaneously (A) and sequentially (B). Arrows indicate the addition of the chemical.

With the combined nitrite and molybdate, the initial decrease of H_2S concentration immediately after addition was more abrupt reaching much lower levels compared when the reagents where applied individually. With the exception of 20 mM nitrite combined with 0.5 mM molybdate, all tested combinations were able to reduce H_2S concentrations to near or below the detection limit (0.4 ppm). This result was not observed when the same levels of nitrite and molybdate were applied to fresh manure individually. Contrary to our expectation, the combined addition of nitrite and molybdate

was not able to maintain the reduced levels of H_2S; an increasing trend in H_2S concentration was observed which eventually levelled off similar to previous cases. The final average concentrations, however, were lower than those observed with nitrite or molybdate added individually and were also dependent on the level of applied reagents. At a constant nitrite concentration increases in molybdate concentration led to lower final concentrations. The same behaviour was observed with increases in nitrite concentration at a constant molybdate concentration. The final concentration of H_2S observed with the simultaneous combination of 100 mM nitrite and 2 mM molybdate was 114±8 ppm. This was only 20% lower than the final concentration of 142±22 ppm obtained with 2 mM molybdate alone and thus one might conclude that application of combined molybdate and nitrite while increasing the cost of the treatment might not offer an advantage as far as the treatment of fresh manure is concerned.

The combined addition of nitrite and molybdate to 3-month old manure had a more pronounced effect (Figure 5.6). The residual H_2S concentration obtained immediately after treatment addition was below the detection limit (0.4 ppm) for all tested combinations. As with the fresh manure, the effect of simultaneous (Figure 5.6-A) and sequential (Figure 5.6-B) addition of nitrite and molybdate on 3-month old manure was similar. Further, comparison of the concentration of H_2S in the control system with the control system in the previous test with reagents added individually showed relatively comparable levels, with 925±66 ppm against 1037±98 ppm respectively.

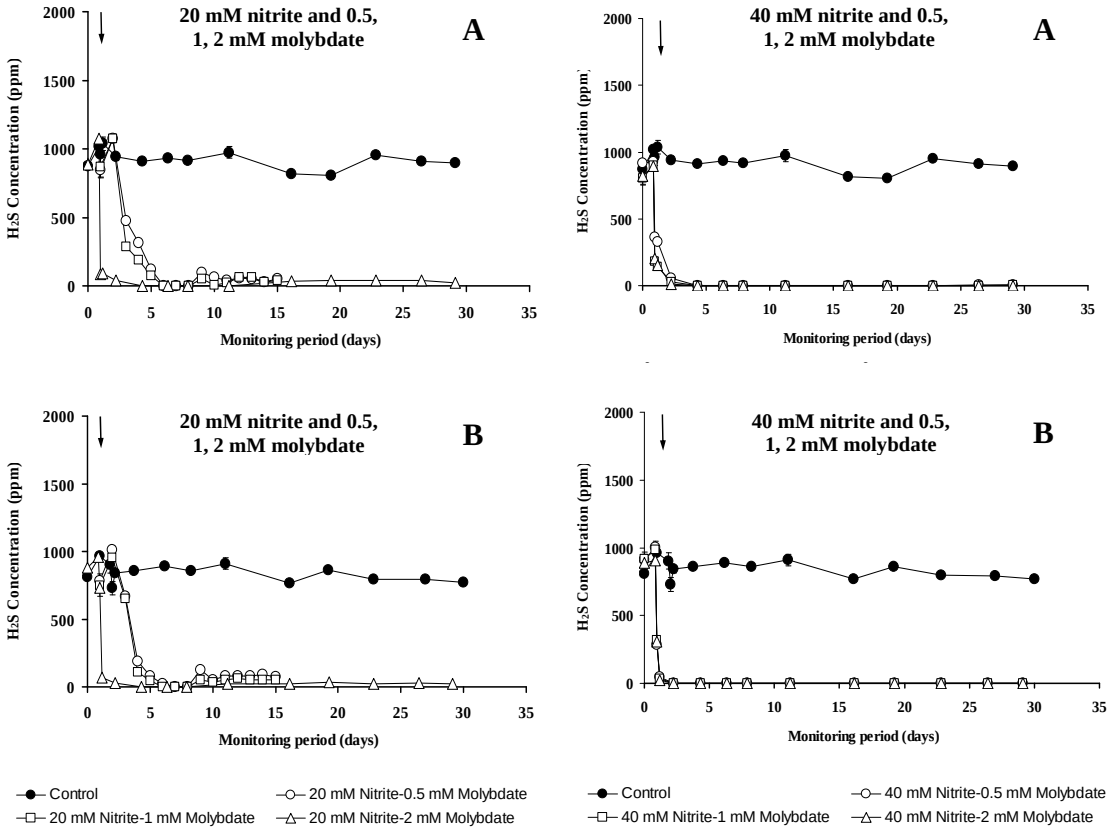

Figure 5.6. Profiles of H_2S concentration in the headspace gas of the serum bottles containing 3-month old manure treated with various amounts of nitrite and molybdate added simultaneously (A) and sequentially (B). Arrows indicate the addition of the chemical.

The simultaneous addition of 20 mM nitrite combined with 0.5, 1 and 2 mM molybdate resulted to final H_2S concentrations of 49±15, 39±23 and 35±8 ppm, respectively, which were lower than those observed with individual reagents. Moreover, the combination of nitrite and molybdate at higher levels (at least 40 mM nitrite and 0.5 mM molybdate) were able to reduce H_2S concentrations below the detection limit (0.4 ppm) and maintained these levels throughout the remaining period of monitoring. The reduction was abrupt and occurred within 36 hours after addition of reagents. These findings indicate that the combined addition of nitrite and molybdate is effective in

eliminating the emission of H_2S from 3-month old manure and may be a feasible option for the treatment of aged (stored) manure. For reference, the complete set of H_2S profiles for all tested conditions in case of simultaneous and sequential addition of nitrite and molybdate to 3-month old manure is presented in Appendix Figure B.5 and B.6 respectively.

5.1.4. Initial addition of nitrite and molybdate (prior to build-up of H_2S)

Additional sets of tests were conducted wherein nitrite and molybdate were added immediately at the beginning of the tests without allowing H_2S concentrations to increase and to stabilize. Similar to the tests with combined nitrite and molybdate addition, only fresh and 3-month old manure were used in these tests. Figure 5.7 shows the profiles of H_2S concentrations from fresh (Panel A) and 3-month old (Panel B) manures with various amounts of nitrite and molybdate applied immediately at the beginning. The complete set of H_2S profiles from fresh and 3-month old manures added with various amounts of nitrite and molybdate at the beginning is presented in Appendix Figure B.7 and B.8. As can be seen from the plots, the levels of H_2S in the control systems for both fresh and 3-month old manures (2247±373 ppm and 867±146 ppm respectively) were considerably lower compared to those in the previous tests. This difference could be attributed to the variation in the properties of the manure as a different batch of manure samples was used in these tests.

The profiles of H_2S concentrations from fresh and 3-month old manures were observed to have a similar trend. The initial increase in H_2S concentration before reaching stabilization was hampered by the immediate application of nitrite and

molybdate. The individual characteristic effect of nitrite and molybdate was evident in these tests. Even with low initial H_2S concentration during addition, nitrite was not able to maintain this level and H_2S concentration increased which eventually levelled off with final concentration depending on the amount of added reagent. It was only with 120 mM nitrite (the highest level of nitrite treatment) reduced levels of H_2S were persistent throughout the monitoring period for both fresh and 3-month old manure.

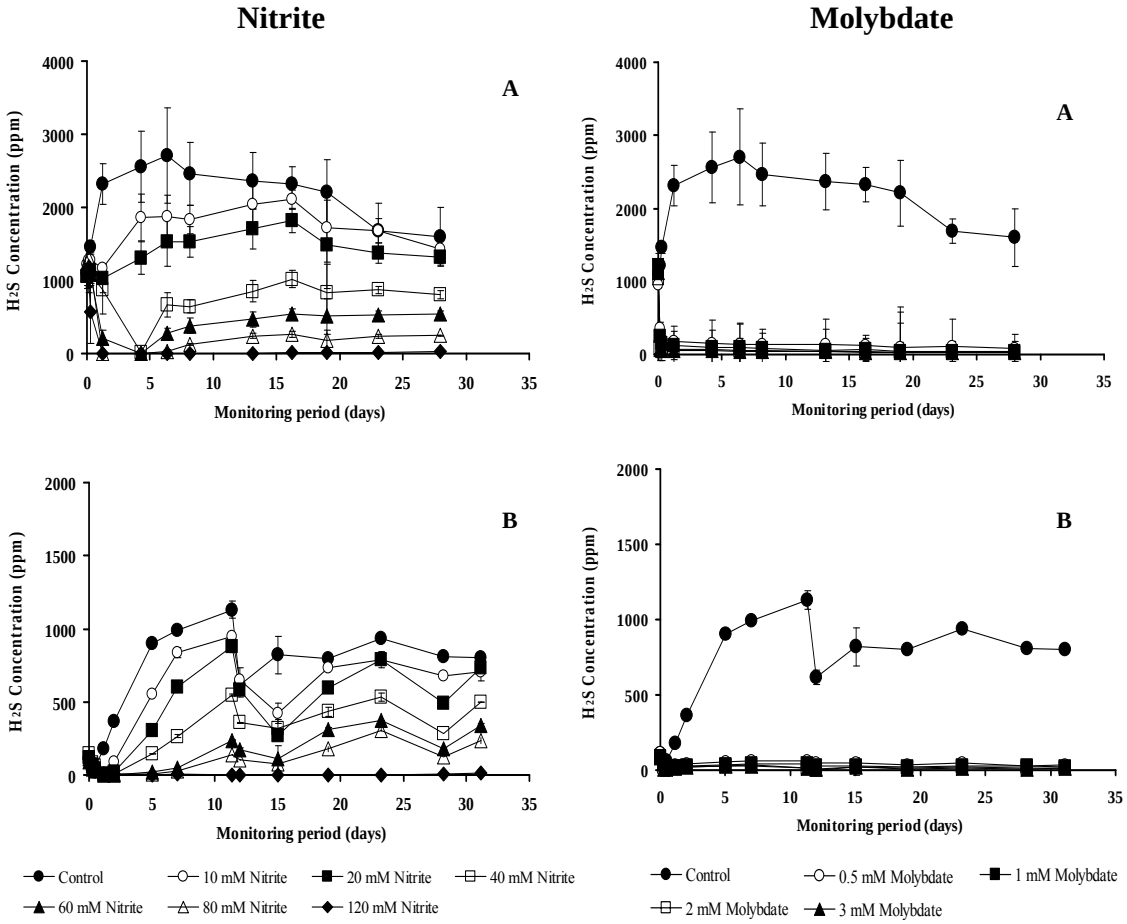

Figure 5.7. Profiles of H_2S concentration in the headspace gas of the serum bottles containing fresh (A) and 3-month old (B) manures applied with various amounts of nitrite and molybdate at the beginning.

On the other hand, the effect of molybdate was consistent with both fresh and 3-month old manures. All molybdate levels (0.5-3 mM) were able to prevent the increase of H_2S at the beginning and maintained it throughout the remaining period of monitoring. For instance, the average concentration of H_2S after the addition of molybdate until the end of the test using 0.5 mM and 3 mM was 140±37 ppm and 38±12 ppm with fresh manure and 42±13 ppm and 15±7 ppm with 3-month old manure, respectively. Moreover, it was observed that the final concentrations of H_2S in both fresh and 3-month old manures were lower compared to those when nitrite and molybdate were added individually and after allowing build-up of H_2S in the headspace. This finding suggests that addition of nitrite and molybdate at the beginning would be a more effective approach since it prevents the increase of H_2S in the first place especially with molybdate treatments. However, it can also be speculated that this result was due to the lower levels of H_2S emitted from the samples. Nonetheless, the effect of molybdate addition was pronounced and most likely similar results would be produced even at higher levels of H_2S.

The results from the laboratory scale tests in closed systems showed that the extent of H_2S emission and the required levels of nitrite and molybdate were both dependent on the manure age. Fresh manure emitted the highest level of H_2S and the level of emission decreased as manure age increased. This led to the decrease in the required level of chemical reagents needed to control the emission of H_2S as manure age increased. Similarly, when equal levels of chemicals were used, lower concentrations of H_2S were observed in the samples taken from aged manure. Further, the synergistic effect of the nitrite and molybdate was only observed with 3-month old manure. Comparison

with the effects of nitrite and molybdate showed a major distinction in their impact on H_2S emission. Application of nitrite initially led to a drastic decrease in emission of H_2S. However, following a lag period which was dependent on the manure age, the emission of H_2S resumed, albeit the final concentration of H_2S in the headspace gas of the treated system was always lower than that in the untreated system. This was not the case with molybdate and apart from one exception (fresh manure treated with 0.5 mM molybdate), H_2S emission did not resume even over an extended period of six months. Molybdate was deemed to be a more suitable treatment and hence, was only used in the semi-pilot and room scale tests.

5.2. Semi-pilot scale tests

The concentrations of H_2S in the gas samples collected from the peripheral and central sampling lines installed on the semi-pilot open top container treated with various amount of molybdate, as well as untreated container (control) are shown in Figure 5.8. Each data bar represents the average H_2S concentrations of two samples collected from each sampling line and the error bar represents the corresponding standard deviation. A technical problem occurred during sampling of the containers treated with 0.05 and 0.1 mM molybdate on day 10 and proper collection of gas samples was not possible, hence the data is not included. In the control system variation in concentration of H_2S were observed when the results of three sampling events were compared. The respective average H_2S concentration obtained from the central and peripheral lines was 831 and 734 ppm on day 10 which decreased slightly to 805 and 675 ppm on day 20 and then increased back to 857 and 792 ppm on day 30. Statistical analysis, however, showed that

these variations in time were not statistically significant (P>0.05). This result indicates that the H_2S emission from the control system upon agitation of the manure was relatively stable when sufficient interval (10 days) was allowed between two consecutive sampling events. The time interval was sufficient to allow stabilization of manure and accumulation of sufficient dissolved sulphide for the next sampling event. The average H_2S concentration throughout the three sampling events (days 10, 20 and 30) was 734±59 and 831±26 ppm at the perimeter and centre of the control container, respectively. Generally, the levels of H_2S measured from the centre of the container were higher than those obtained from the perimeter. This could be due to the larger space of sampling in the centre than those at the perimeter near the container edge. However, the differences were found to be statistically insignificant (P>0.05).

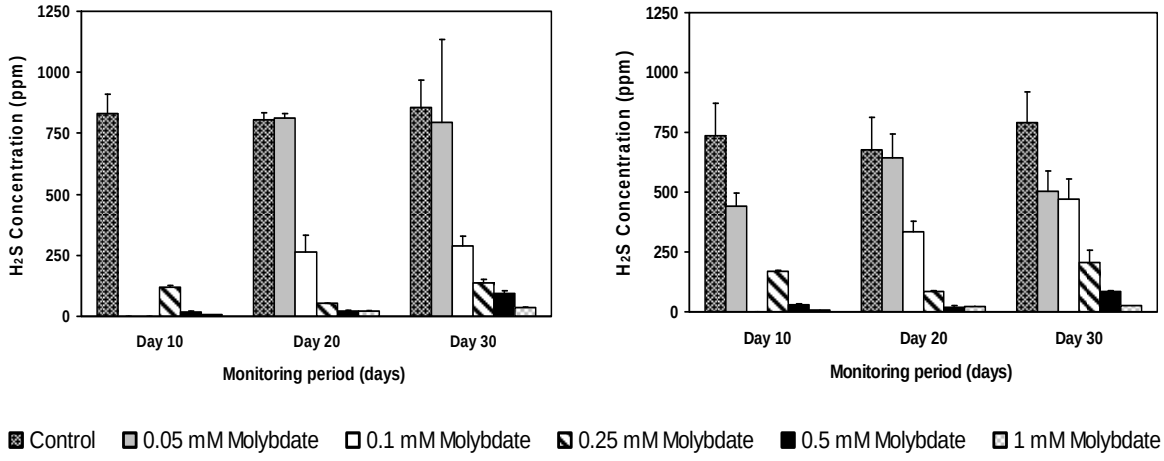

Figure 5.8. H_2S concentration in the headspace gas samples collected from the centre and perimeter of the open tubs containing fresh manure treated with molybdate.

As shown in Table 5.2, the concentration of H_2S in the gas samples collected from the container with manure treated with various amounts of molybdate was significantly

lower than that of the control system ($P<0.05$, ANOVA with repeated measures test, SAS software, SAS Institute Inc., NC, USA). Furthermore, increase of molybdate concentration, irrespective of sampling location, led to lower H_2S concentrations. For instance, on day 30, the average concentrations of H_2S in the tubs added with 0.05, 0.1, 0.25, 0.5 and 1.0 mM Mo were 504±84, 469±85, 206±51, 86±1 and 24±1 ppm respectively from the centre and 796±338, 289±39, 138±12, 94±10 and 36±4 ppm respectively from the perimeter. Throughout the three sampling events, the average reduction percentage of H_2S emission using 0.05, 0.1, 0.25, 0.5 and 1.0 mM molybdate was 27-97%. Similar to the control system, fluctuation in H_2S concentration was observed when the results of three sampling events were compared. A slight increase in the concentration of H_2S on days 20 and 30 was observed for all treated systems but levels were still significantly lower than those from the control. For instance, H_2S concentration in the tub treated with 1.0 mM Mo increased to around 20 ppm and 30 ppm on Days 20 and 30 respectively. However, with the addition of 0.05 mM Mo, a substantial increase in H_2S emissions was observed wherein its concentration levelled with the control especially on day 20.

Table 5.2. Mean H_2S concentrations obtained from the centre and perimeter of open top containers containing the untreated and treated manures with various amounts of molybdate over the three sampling events.

	Centre (ppm)	**Perimeter** (ppm)
Control	831.07	733.60
0.05 mM Molybdate	803.60	529.67
0.10 mM Molybdate[1]	276.03	402.51
0.25 mM Molybdate	103.50	153.08
0.5 mM Molybdate	45.64	44.74
1.0 mM Molybdate	22.15	17.70

[1] Data from 0.1 mM Molybdate were not used in the analysis due to lack of observations, n=4

Comparing the extent of H_2S emissions obtained in these tests to those from the laboratory scale tests, the concentrations measured from the open top containers were significantly lower than those from the laboratory scale tests. As indicated previously, the average level of H_2S from the open top container with untreated fresh manure was 831±26 and 734±59 ppm from the centre and perimeter respectively while that from the serum bottles containing fresh manure was 4856±460 ppm. Consequently, lower concentrations of H_2S obtained from the open top containers required lower levels of molybdate to control its emissions compared to those applied in the serum bottles. For instance, the average final concentration of H_2S in the headspace gas of serum bottles containing fresh manure of 142±22 ppm was obtained using 2.0 mM molybdate while at about the same average final concentration in the open top containers (138±12 and 206±51 ppm from the perimeter and centre respectively), only 0.25 mM molybdate was needed.

Differences in physical appearance were observed between manure treated with various amounts of molybdate and that in the control system. Manure in the control system appeared grayish black in color while manure applied with 0.05 mM molybdate appeared brownish black; similar differences in appearance of the manure samples were observed in the laboratory scale tests. Moreover, the degree of brownish color in the treated manure was more pronounced with higher levels of molybdate. This change of colour could be potentially due to oxidation of sulphide and formation of other sulphur compounds. Analysis of properties of manure treated with 0.25 and 1.0 mM molybdate (the median and highest level of molybdate treatment) as well as that of the untreated manure from the open top containers are shown in Table 5.3. As with the properties of

manure from the serum bottles in the laboratory scale tests, apart from the content of molybdate in the manure, all other properties between the manure samples analyzed were found to have no major differences. This finding again indicates that the treatment had little impact on the nutrient properties of the manure.

Table 5.3. Properties of fresh manure treated with 0.25 and 1.0 mM molybdate as well as that in the untreated system in the open top containers (unless otherwise stated all the properties are in mg/kg dry manure).

Property	Control	0.25 mM Mo	1.0 mM Mo
TOC	16800	12600	19900
Ammonia	2400	2500	2600
Kjeldahl N	3600	3300	4200
Protein	22500	20600	26300
P	1430	836	1490
K	3240	3020	3500
S	428	415	659
Nitrite	0.5	1.55	4.9
Mo	<1	20.5	137
Total Solids (%)	4.4	3.5	5.4
pH	7.2	7.3	7.3

n=1

5.3. Room tests

As described in the experimental procedures (Section 4.3.2), preliminary tests indicated that H_2S emissions in the chambers were much lower than that observed in the open top containers and serum bottles. Therefore, a lower molybdate concentration (0.10 mM) was used in the room tests. Moreover, the preliminary test provided the opportunity to establish and modify the sampling protocol adapted for the room tests, such as the position of sampling lines, sampling duration and the method used for manure agitation. Following these preliminary tests, two trials were conducted. The results and observations from these trials are presented in the following sections.

Figure 5.8 shows the H_2S content of the gas samples collected at 2 and 5 minutes after initiation of the manure agitation in the control chamber (untreated manure) and in the chamber in which manure was amended with 0.1 mM molybdate for the first and last sampling events conducted on day 28 and 48 of the first trial, respectively. The H_2S concentrations observed at 10 and 15 minutes after the start of agitation are not presented since their levels are much lower than those at 2 and 5 minutes (e.g. highest H_2S concentration at the pit level in the control chamber at 10 and 15 minutes was 1.6 ppm compared to 88.4 ppm at 2 minutes). The concentrations at 10 and 15 minutes, however, are presented in Appendix Table B.1.

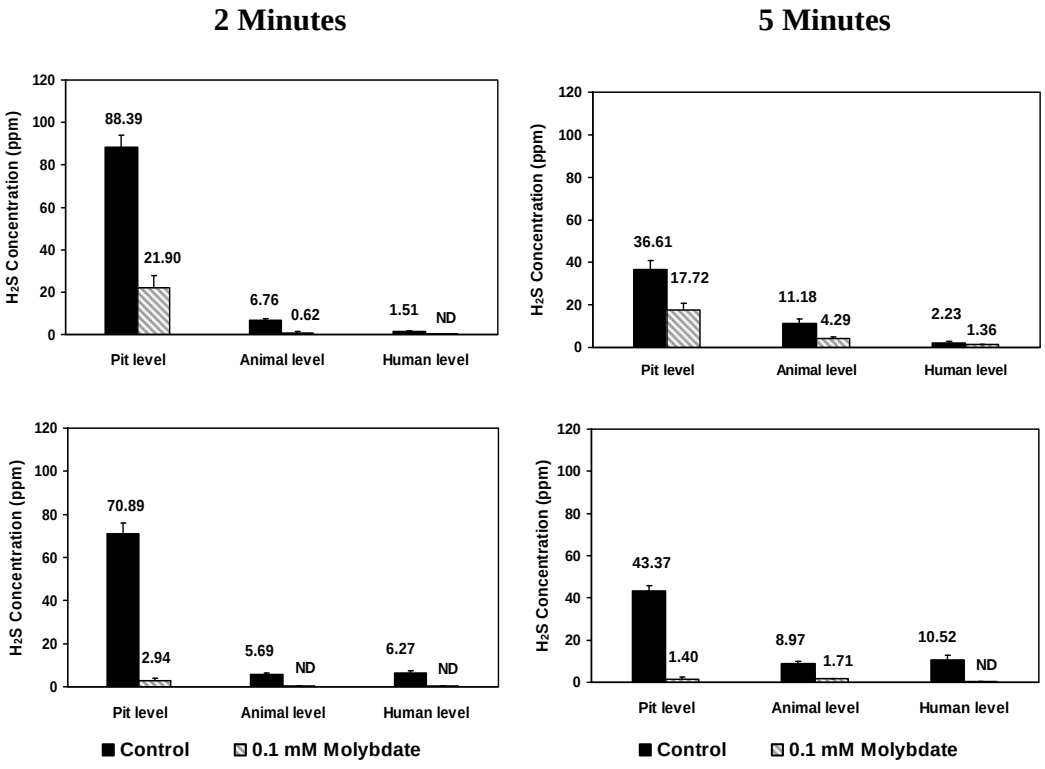

Figure 5.9**.** H_2S concentration in the gas samples collected in the room scale experiments from the untreated manure and manure treated with 0.1 mM molybdate at 2 and 5 minutes after the start of agitation during the first (A) and third sampling events (B) in the first trial. (ND: not detected).

Due to a technical difficulty with the submersible pump used for the agitation of the manure, the second sampling event was unsuccessful, thus no data was included. Also, comparison of H_2S concentrations obtained from the two adjacent pit level lines showed that the H_2S concentrations from pit level 1 (line farther from the chamber wall) was significantly higher than the concentrations obtained from pit level 2 (line closer to the wall) ($P<0.05$, ANOVA with repeated measures test, SAS software, SAS Institute Inc., NC, USA) due to the effect of overall ventilation airflow pattern within the chamber. Hence, the higher concentrations of H_2S from pit level 1 were chosen to represent the pit level readings in Figure 5.8. The numbers on each bar represent the average concentration obtained from multiple samples and error bar is the associated standard deviation.

As shown in Figure 5.8, addition of 0.1 mM molybdate led to much lower H_2S concentrations in all sampling elevations. For instance on the first sampling event (day 10), H_2S concentration in the pit, animal and human levels in the control chamber after 2 minutes of agitation was 88.4, 6.76 and 1.5 ppm, respectively, while the corresponding concentrations in the treated system were 18.8, 0.6 and below the detection limit (<0.4 ppm), respectively. The decrease was more pronounced during the third sampling event with H_2S concentrations in the pit, animal and human levels being 2.9 ppm and not detectable for the other two positions, respectively. The mean concentration of H_2S in the chamber with added molybdate was found to be significantly lower than those observed in the control chamber ($P<0.05$, ANOVA with repeated measures test, SAS software, SAS Institute Inc., NC, USA). Moreover, change in the levels of H_2S with time was observed in both chambers. During the third sampling event, H_2S concentration of gases

collected in the control chamber at 2, 5, 10 and 15 minutes after the start of agitation were 70.9, 43.4, 2.8 ppm and not detectable, respectively. In the treated chamber, concentrations measured at 2, 5, 10 and 15 minutes after the start of agitation during the third sampling event were 2.9, 1.4, ppm and not detectable for the last two samples, respectively.

In the second trial, despite the exactly the same parameters and procedures applied as with the previous trial, the manure collected in the tubs had a different consistency, appeared to contain more solids, thus creating difficulties in agitation during sampling. . Furthermore, drying and formation of crust on the manure surface was evident. As a result, the submersible pump used for agitation of manure during the sampling was not very effective in creating sufficient flow and mixing of manure was not achieved, which was the potential reason for lower levels of H_2S both in the control and treated chambers when compared with previous trials, particularly for the first two sampling events. As the trial progressed, the manure consistency became more like those observed in the previous trial (more slurry-like), thus by the third sampling event, a reasonable level of mixing was achieved and consequently higher H_2S concentrations were obtained (Figure 5.9). Nonetheless, for this trial, H_2S concentrations from the chamber with the treated manure obtained at 2 and 5 minutes after the start of agitation were lower compared to those from the control chamber, which is consistent with the results from the previous trial. For instance in the first sampling event, concentration of H_2S in the pit level in the control and treated chambers were 20.9 and 3.0 (at 2 minutes) and 14.3 and 3.3 (at 5 minutes), respectively. Moreover, the decline in H_2S levels with increase in sampling elevation was also observed in the three sampling events. For

reference, the concentrations of H_2S measured after 10 and 15 minutes are shown in Appendix Table B.2.

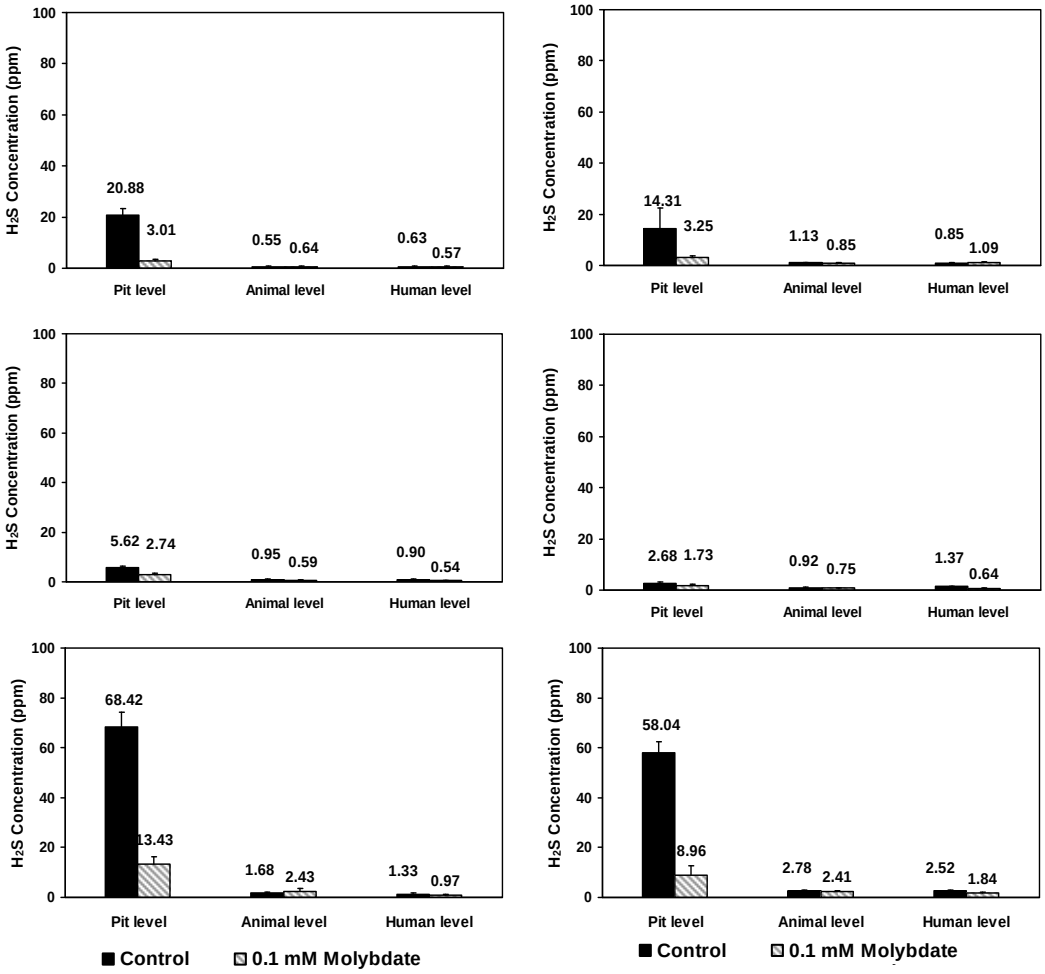

Figure 5.9. H_2S concentration in the gas samples collected in the room scale experiments from the untreated manure and manure treated with 0.1 mM molybdate at 2 and 5 minutes after the start of agitation during the first (A), second (B) and third sampling events (C) in the second trial (ND: not detected).

As described earlier, during the trials some unforeseen technical difficulties were encountered which caused variation in the level of emitted H_2S in both trials. The low

level of H_2S emission during the sampling events in trial 2 was due to inadequate agitation of manure or low level of manure production in this trial. The problems during manure agitation were mainly caused by pump failure wherein flow of manure became intermittent when the pump was no longer able to handle the excessive thickness of the manure slurry. During the second trial, manure produced in both chambers appeared to be more viscous and contained more solids, which was evident from manure surface crusting, at a level much higher than that observed during the first trial. Lower manure production in the second trial could also have contributed to the low levels of emitted H_2S.

Despite these unforeseen problems which were beyond the control of investigators, results from these trials were in agreement with those obtained in laboratory and semi-pilot scale systems and indicated that addition of molybdate reduced the emission of H_2S from manure. This was evident from the analysis of the mean H_2S concentrations obtained at the different sampling elevations in both control and treated chambers for these two trials, as shown in Table 5.4. Statistical analysis of the data at all sampling elevations and times indicated that the levels of H_2S in the treated chamber were significantly lower than those in the control chamber ($P<0.05$; ANOVA with repeated measures test, SAS software, SAS Institute Inc., NC, USA). Furthermore, it was found that the concentrations of H_2S measured at different sampling heights were significantly different from each other ($P<0.05$; ANOVA with repeated measures test, SAS software, SAS Institute Inc., NC, USA)), with the highest concentration of H_2S was observed at the pit level and decreased with the increase in sampling elevation. The decrease of H_2S concentration with spatial elevation in the rooms is most likely due to the

fact that H_2S is heavier than air, and that the ventilation air diluted the emitted gas as it moved away from the source (pit). Analysis of the gas samples taken in each sampling event over a period of 15 minutes revealed that for a fixed sampling location H_2S concentration decreased as sampling time progressed. The decrease in H_2S content of the emitted gases with time is expected since agitation of the manure was stopped after 5 minutes, while ventilation system was kept running. All concentrations measured from both the control and treated chambers at 10 minutes after agitation were under 3 ppm and almost all samples at 15 minutes were below the detection limit.

Table 5.4. Mean H_2S concentrations obtained from the different sampling levels in both the control and treated chambers at 2 and 5 minutes in two trials.

Sampling level	2 minutes		5 minutes	
	Control	Treated	Control	Treated
Pit	47.63	7.96	33.49	6.57
Animal	3.18	0.99	4.66	1.61
Human	2.38	0.64	3.21	1.08

The highest concentrations of H_2S (88.4±5.7 ppm) measured in the gases emitted from untreated manure in the room tests (at the pit level for the first trial) were significantly lower than the levels observed with untreated fresh manure in the open top containers (831±26 ppm) and much lower compared with untreated fresh manure in the closed serum bottles (4856±460 ppm). These lower levels of H_2S in open system are expected as manure is exposed to air and anaerobic conditions might not prevail throughout the manure. This in turn negatively influences the activity of the strictly anaerobic SRB. Moreover, in a closed system, the produced H_2S that diffuses from the liquid phase accumulates in a confined volume in the headspace. In an open system, the diffused H_2S is continually diluted with air and removed from the airspace by the

ventilation system. Spikes of H_2S were only experienced as a result of manure agitation which was induced intentionally for this investigation. Finally, the results of the trials in the open top container and room scale chambers revealed that molybdate at levels much lower than that required for the closed system (0.1-0.25 mM as opposed to 2 mM) controlled the emission of H_2S in these systems. It should be pointed out that the level of emitted H_2S during draining and clearing of the manure from the pits in a swine barn may be higher than those observed in the present work and may linger for extended periods. This is due to larger number of the pigs and higher volumes of produced manure in actual production rooms, more intense mixing of manure during the drainage and cleaning, and reduced significantly ventilation rates at certain months of the year. Moreover, the technical difficulties experienced during the room tests is unlikely to be encountered in real barn conditions due to better consistency and larger volumes of manure.

Continuous monitoring of the air leaving each chamber for NH_3 concentration indicated that addition of molybdate did not impact the emission of NH_3 ($P>0.05$; paired t-test, Excel Software, Microsoft Corporation) with the average concentrations over 48-day monitoring period for the control and treated chambers being 6.62±1.47 and 6.56±1.37 ppm, respectively, for both trials (Figure 5.10, Panel B). However, temporary spikes in NH_3 concentration were observed when manure was agitated during the sampling events. Some of the spikes, especially those measured in the control chamber, triggered the alarm level (>35 ppm) of the PAC 7000 ammonia monitor (Draeger Safety Inc, Pittsburgh, PA, USA) placed near the pit surface of the chamber during sampling as an added monitoring device. Further, comparison of CO_2 levels in the air leaving the control and treated chambers revealed no significant difference ($P>0.05$; paired t-test,

Excel Software, Microsoft Corporation), with average values throughout the 48-day monitoring period being 665.83±113.71 and 643.63±133.49 ppm, respectively, over these two trials (Figure 5.11, Panel B).

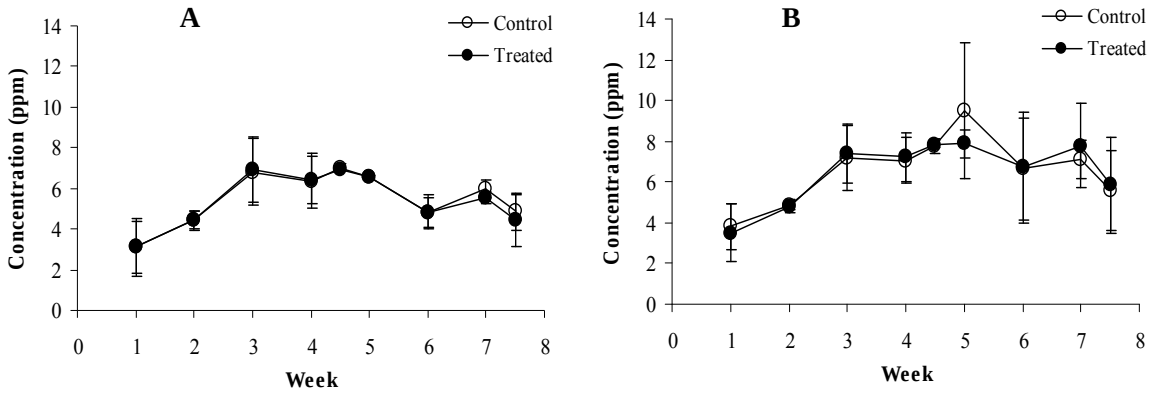

Figure 5.10. Ammonia concentrations measured at the (A) inlet and (B) exhaust of the environmental chambers over the two trials.

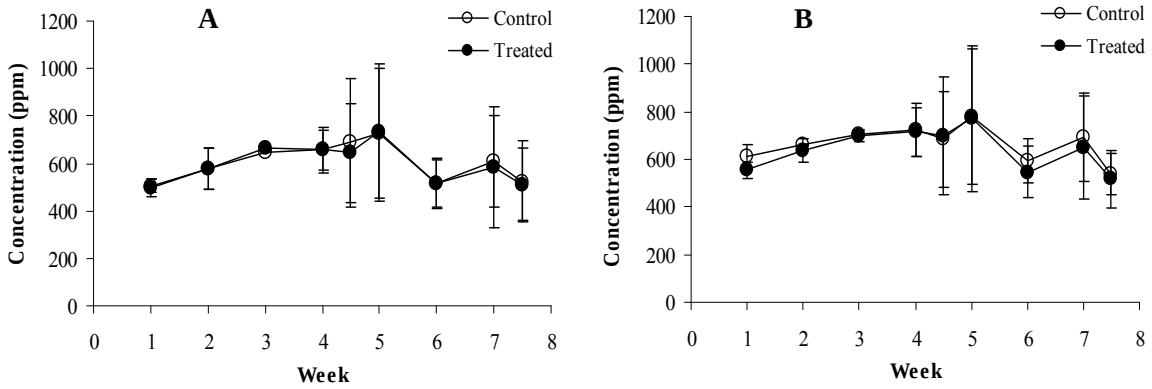

Figure 5.11. Carbon dioxide concentrations measured at the (A) inlet and (B) exhaust of the environmental chambers over the two trials.

The average water usage of the pigs in the control and treated chambers were 4.1±1.2 and 4.9±1.2 and 4.6±1.1 and 3.9±1.1 L/day-pig during the first and second trials, respectively. Although water usage in the treated room was slightly higher than that in the control room, this difference was not reflected in the manure production and weight

gain of the pigs. There was no significant difference in manure production between the pigs in the control and treated chambers having average daily production rates for the entire 48 day trial period of 26.7±8.5 vs. 28.2±7.9, and 21.5±7.1 vs. 23.0±8.8 L/day during the first and second trials, respectively ($P>0.05$; paired t-test, Excel Software, Microsoft Corporation). Moreover, no significant difference in average daily gain (ADG) between pigs in the control and treated chambers was also observed ($P>0.05$; paired t-test, Excel Software, Microsoft Corporation) with average values of 0.96±0.06 vs. 0.94±0.06, and 0.92±0.10 vs. 0.89±0.16 kg/day-pig measured during the first and second trials, respectively. Further, in terms of average daily feed intake (ADFI) of pigs, no significant difference was observed between the ADFI of pigs in the control and treated chambers ($P>0.05$; paired t-test, Excel Software, Microsoft Corporation) with average values of 2.1 vs. 2.1, and 2.0 vs. 2.0 kg/day-pig obtained during the first and second trials, respectively.

5.4. Manure properties and small scale application of manure to soil (soil tests)

A portion of the manure samples collected from the room tests that were used in the soil test was sent for analysis of physico-chemical properties and the results are shown in Table 5.5. As expected the manure sample collected from the treated chamber had significantly higher content of molybdate content. Moreover, it was observed that the amount of sulphur, potassium and sodium were considerably lower in the treated manure. Lower sulphur content could translate to lower H_2S levels produced in manure and lower sodium content indicates lower risk of high excessive sodicity in the soil after manure application. The other properties presented in Table 5.5, such as total nitrogen,

phosphorus, nitrate and total carbon, were similar in the untreated and treated manure. The sulphur, potassium and sodium contents of the treated and untreated manure were different but no concrete explanation could be provided for this discrepency since only one batch of manure samples were analyzed.

Table 5.5. Properties of manure samples collected from the control and treated chambers after the room-scale tests (unless otherwise stated all the properties are in mg/kg dry manure).

	Control	Treated
Ammonia	6500	5890
Total Kjeldahl Nitrogen	9290	8270
Protein	58100	51700
Phosphorus	1850	1710
Potassium	3160	29.1
Sulfur	1120	10.2
Sodium	1220	11.6
Molybdenum	<1	7.22
Nitrate	<0.5	<0.5
Nitrite	0.34	0.28
Total Carbon	48000	52200
Total Solids (%)	12.3	12.5
Moisture (%)	87.7	87.5
Conductivity (uS/cm)	28600	26400
pH	7.19	6.97

n=1

The analysis for physical, chemical and microbial properties of soil core samples collected from the plots on which untreated and treated manures were applied as well as the plot without added manure are shown in Table 5.6. Generally, it was observed that most of the properties analyzed from the top portion of the cores had values higher than those from the bottom cores. This finding is likely due to the fact that most of the humus and organic content are found in the top soil (0-10 cm from the surface). Further, the amounts of soil available nutrients (N, P, K) as well as cation content (Ca, Mg, K, Na) from the soil cores obtained from the plots with applied manure (both untreated and

treated were considerably higher than those from the bare soil cores. This is consistent with the known fertilizer value of manure as a nutrient supplement for the soil, thus manure application is widely practiced by farmers as an alternative to use of chemical fertilizers.

Table 5.6. Physical, chemical and microbial properties of soil core samples.

Analysis	Unit	Untreated Top	Untreated Bottom	Treated Top	Treated Bottom	Bare Soil Top	Bare Soil Bottom
Heterotrophic Plate Count	CFU/g	2.62 x 10^7	2.84 x 10^6	8.03 x 10^7	2.95 x 10^6	6.7 x 10^6	1.13 x 10^6
Molybdenum (Mo)-Total	mg/kg	0.312	0.236	0.403	0.23	0.25	0.209
Total Coliforms	MPN/g	15	7	>1100	93	9	<3
Available Nitrate-N	mg/kg	124	16.5	127	12.3	32.2	11.2
Available Phosphate-P	mg/kg	114	20.2	138	18.1	85.3	23
Available Potassium-K	mg/kg	651	194	545	162	410	172
Calcium	mg/L	406	78	362	57.3	107	55.1
Potassium	mg/L	102	7.7	108	5.8	35.1	6.3
Magnesium	mg/L	113	21.7	103	16.2	28.3	16
Sodium	mg/L	60.4	8.4	62.2	7.3	8.6	8.6
SAR	SAR	0.68	0.22	0.74	0.22	0.19	0.26
% Saturation	%	49	41	52	41	49	39
pH in Saturated Paste	pH	6.44	7.29	6.39	7.39	6.96	7.48
Conductivity Sat. Paste	dS m^{-1}	3.2	0.62	3.1	0.46	0.89	0.45

n=1

Comparison of properties between the soil cores from plots applied with untreated and treated manure showed no major differences except for the presence of total coliforms. The total coliform population in the top soil core from the treated plot (>1100 MPN/g) was significantly higher than the population in the untreated plot of the same soil core section (15 MPN/g). With no readily apparent cause for this difference, it could only be speculated that this difference is due to the high variability of manure and soil properties, as well as possible contamination of specific samples during field sampling

and in handling and analysis at the commercial laboratory which performed this procedure. Although utmost care was observed in conducting the field test and in collecting the samples, the analysis was done on only one composite sample from each soil core section of each plot, thus this observation can not be verified with a duplicate sample.

In terms of molybdate content, as expected, the soil cores from the plot applied with the treated manure (0.40 mg/kg) was slightly higher than those from the plot with the untreated manure (0.31 mg/kg) and bare soil (0.25 mg/kg). Previous studies have shown that health risks due to exposure to molybdenum, specifically sodium molybdate, as well as molybdate toxicity to soil, plants and grazing animals seldom occurs and varies according to crop species (Gupta 1997). A condition known as molybdenosis, wherein molybdenum toxicity associated with copper deficiency could occur, has been reported in ruminants grazing on plants grown on soils with high levels of molybdenum in the range of 100-1000 ppm (Gupta 1997). A study conducted by McBride et al. (2000) revealed excessive uptake of molybdenum into red clover (*Trifolium pratense* L.) grown in soil amended for 20 years with sewage sludge which contained 3 mg molybdate per kg of soil. According to McBride et al. (2000), total molybdenum concentration found in the agricultural soils in eastern North America normally range from 0.5 to 2 mg/kg. As indicated earlier, the molybdate content of the soil core from the plot applied with the treated manure was 0.40 mg/kg, which is way below the levels that could cause molybdenosis.

Exposure of workers and animals to molybdate during application of the treatment is also a potential concern. Sodium molybdate has a median lethal dose (LD_{50})

of 4 g/kg body weight (CCOHS, 2009). As such, for a 50 kg animal, as much as 200 g of the chemical agent is needed for a lethal dose. In the room tests, the total amount of sodium molybdate required for the treatment was close to10 g which is significantly smaller than the lethal amount. Nonetheless, taking measures to ensure that animals are not exposed to the applied solution or the treated manure slurry, and the use of protective clothing and equipment by the workers are essential to eliminate or minimize exposure during the preparation and application of the molybdate solution.

5.5. Feasibility study

Following the completion of room scale experiments, a preliminary feasibility study on application of molybdate in a typical swine operation was carried out. The main components used in this calculation included the costs associated with material (Na-molybdate), labour and purchase of the required equipment with the details listed in Table 5.7. The calculations were based on a 300-sow operation with 72-head capacity grow-finish rooms in which pigs are kept for 16 weeks until moved out for market. Following current production performance of typical operations across the Canadian pig industry, each sow was estimated to produce 25 piglets per year, so a total of 7500 grow-finish pigs per year were assumed to be handled. In this analysis, it was assumed that the treatment was applied only at the grow-finish stage of production, thus the treatment cost per pig was calculated using the data for one complete growth cycle in a grow-finish room. Throughout the 16-week growth period in this production stage it was estimated that 6 pit-pulling (or draining) sessions would be carried out at 2-3 weeks intervals. Application of the treatment will be done once every 10 days before each pit-pulling session, the same

time interval between treatment application and manure agitation employed during the room tests. Because the manure pits will then be cleared of treated manure after each pit-pulling session, the treatment solution will need to be re-applied after each pit-pulling session. Each production room has a single pit channel which was assumed to be completely empty after each pit pulling event. The volume of the produced manure was estimated based on the average rate of manure production per pig for different weight classes. For pigs weighing less than 68 kg, the average manure production rate was 2.27 L/day, while pigs weighing 68 kg and above produced manure at an average rate of 6.36 L/day (MWPS, 1993). The volume of manure in the pit was then determined by getting the total manure produced by 72 pigs. To distinguish the weigh classes of pigs, their weights were initially determined using the average daily gain of pigs (0.9 kg/day) obtained during the room trials. Pigs were assumed to have starting weights of 20 kg when moved into the room.

The calculations for determining the amount of molybdate solution to be applied to the manure and the corresponding amount of sodium molybdate salts to be prepared followed the same procedure of calculations employed in the serum bottle tests as presented in Appendix A. The volume of molybdate solution was first determined based on the total amount of manure in the pit. The concentration of molybdate solution was selected as 20 mM. The amount of molybdate salts to be used in preparation of the solution was then determined and its corresponding cost was calculated. For the calculation of labour cost, the duration of treatment application was estimated based on the trials performed in the chambers. These trials indicated that it would take 30 minutes to prepare and apply the treatment to each room which would be a total of 3 hours per

production cycle per room. From this information, the total labour cost for the application of the treatment was determined. Furthermore, the capital cost associated with the treatment approach was calculated using the price of the equipment used during the room scale trials since same type of equipment with the same size can be used in a large scale room.

Table 5.7. Details of various items and information used in the cost estimation for control of H_2S emission with molybdate, applied in the grow-finish stage of the operation.

Operational information	
Growth-finish cycle length	16 weeks
Number of pit pulling to clear manure (number of molybdate applications per cycle)	6
Labour hours required for molybdate application per cycle	3
Number of pigs per cycle in each room	72
Average daily weight gain	0.9 kg/day
Manure production rate (MWPS, 1993) weight range: 30-68 kg weight range: 68-90 kg	 2.27 L/day 6.36 L/day
Target sodium molybdate concentration in the manure	0.1 mM
Total weight of applied molybdate per cycle	0.82 kg
Associated costs	
Molybdate (unit price, kg)	$41.28
Labour (hourly wage)	$13.00
Operating costs per pig	**$1.01**
Total capital costs for scale, handheld mixer, sprayer, containers	$600.00
Capital costs per pig*	**$0.016**
Total costs per pig	**$1.026**

*Equipment life span: 5 years; Number of finished pigs per year: 7500; All costs in CAD$.

The result of this cost study indicated that the cost associated with this H_2S emission control with molybdate applied in the finishing stage will be around CAN$1.065 per market pig, which amounts to less than 1% of the average total cost of production of about CAN$167.36 (MAFRI, 2008). The details of the calculations for this cost study are presented in Appendix C.

6. CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE WORK

Conclusions

Based on the results of the studies in the laboratory, semi-pilot and room scale tests, the following conclusions can be drawn:

1) The laboratory tests showed that the extent of H_2S emission from swine manure and the required level of molybdate and nitrite for the control of this emission depend on the manure age, and an increase in manure age (storage period) leads to lower H_2S emissions and lower quantities of the chemical agents required to control these emissions. With fresh 1, 3, and 6-month old manures, average H_2S concentration in the headspace gas of the closed systems were 4856±460, 3431±208, 1037±98 ppm, and non-detectable (<0.4 ppm), respectively.

2) The addition of nitrite initially led to lower levels of H_2S in the emitted gases but its effect was only temporary and was not as persistent as molybdate which maintained a low level of H_2S over an extended period (at least six months). The level of molybdate required to control H_2S emissions from fresh, 1-month and 3-month old manures was 2.0, 1.5 and 1.0 mM respectively.

3) Simultaneous addition of nitrite and molybdate did not offer any advantage in reducing the emission of H_2S from the fresh manure but had a synergistic effect on reducing the emission of H_2S from aged manure.

4) The emission of H_2S produced from untreated manure in open large scale systems are significantly lower than in closed small scale systems. Concentrations of H_2S from

untreated manure in the semi-pilot scale open containers and specifically designed environmental chambers were 831±26 and 88.4±5.7 ppm respectively while in the serum bottles was 4856±460 ppm.

5) The results of room tests confirmed that the addition of molybdate at levels much lower than that required for the closed system (0.1 mM as opposed to 2 mM) controlled the emission of H_2S effectively under conditions close to that of an operational swine barn.

6) A preliminary feasibility study for an average size sow operations (7500 finished pigs per annum) indicated that costs associated with the application of molybdate to control H_2S emission amounted to around CAN$1.00 per market pig, which represents less than 1% of the average total production cost.

7) Analysis of the nutrient properties of the manure collected from the room scale tests, showed no major differences between the treated and untreated manure. However, an exception would be the potassium content wherein the treated manure had significantly lower levels than that of the untreated manure, possibly due to wide variability in the properties of manure as previously documented in related studies.

8) The application of manure to undisturbed soil plots revealed that the nutrient properties of the soil on which treated manure was applied mostly not adversely affected by the treatment process. No major differences were observed among the soils exposed to treated and untreated manure and that the land application of manure

treated with 0.1 mM molybdate did not raise the level of molybdenum in the soil to levels which could cause potential toxicity to both plants and grazing animals.

Recommendations

1) Based on the results of the laboratory scale tests, it was speculated that addition of nitrite or molybdate contributed to control of H_2S emission from manure through two mechanisms which occur sequentially. In the first mechanism, addition of nitrite or molybdate would catalyze the chemical oxidation of sulphide (spontaneous oxidation) which results in a sharp decrease in H_2S concentration over a short period of time. In the second mechanism the known inhibitory effect of nitrite and molybdate hinders the activity of sulphate reducing bacteria (SRB) and biogenic production of sulphide. Exact mechanisms of nitrite and molybdate mediated control of H_2S emission need to be established through additional experimental work. This could be done by conducting investigation on spontaneous chemical oxidation of H_2S either in the gaseous form or sulphide dissolved in aqueous phase in the absence and presence of nitrite and molybdate to verify the potential catalytic effects of these compounds on sulphide oxidation.

2) A detailed investigation on the composition of microbial community, especially SRB, prior and after treatment of the manure with nitrite and molybdate will assist in verifying the inhibitory effects of these compounds on SRB and emission of H_2S.

3) Based on the results observed in both semi-pilot and room scale tests, lower levels of molybdate (<0.1 mM) might prove effective in control of H_2S emission. This possibility which could reduce the treatment cost should be investigated.

4) In the completed tests application of treatment to the manure was done at the early stage of the tests to assess the effectiveness and persistency of this approach. However, concentration of H_2S in ventilated production rooms is normally low (<1 ppm) and high levels of H_2S are encountered mainly during manure agitation (plug pulling, power washing, etc). Therefore, as an alternative, addition of these inhibitors could be carried out 24-48 hours before draining of the manure in which case both nitrite and molybdate would be effective. This will take advantage of the more pronounced effect of nitrite in instantaneously decreasing emitted sulphide but on a temporary basis. Therefore, additional studies on the timing of the treatment application might be worthwhile.

5) Application of this treatment approach in an actual swine barn is recommended to identify any unforeseen technical and practical problems and to conduct a more detailed feasibility study.

6) Large scale land application of the treated and untreated manure and detailed analysis of the soil samples, especially tests focusing on molybdate toxicity and nutritional values, are also recommended. Analysis of manure and soil properties should be done on a larger number of replicates. It would be beneficial to conduct some of these tests on a land with growing plants as well.

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8. APPENDICES

A. Sample computation

Appendix A.1. Example computation for determining amount of nitrite and molybdate salt to be diluted in RO water to obtain a concentrated solution of nitrite or molybdate.

For a 25 mL of a 200 mM concentrated nitrite solution, 0.345 g of sodium nitrite salts was needed. Likewise, for 50 mL of concentrated molybdate solution, 0.424 g of sodium molybdate dihydrate salts was added.

$$X_i = MW \times C_i \times V_w$$

where:

MW = molecular weight of chemical agent, g/mol
C_i = concentration of chemical agent in RO water solution, mM or mmol/L
V_w = volume of RO water
X_i = amount of chemical agent to be added in RO water, g

Example computations for determining amount of chemical agent in preparing a concentrated solution:

- For a 25 mL of 200 mM concentrated NO_2 solution:

$$X_i = \frac{69\,g}{mol} \times \frac{200\,mmol}{L} \times \frac{1\,mol}{1000\,mmol} \times 25\,mL \times \frac{1\,L}{1000\,mL}$$

$$\underline{X_i = 0.345\,g}$$

- For a 50 mL of 35 mM concentrated Mo solution:

$$X_i = \frac{242\,g}{mol} \times \frac{35\,mmol}{L} \times \frac{1\,mol}{1000\,mmol} \times 50\,mL \times \frac{1\,L}{1000\,mL}$$

$$\underline{X_i = 0.424\,g}$$

Appendix A.2. Example computation for determining amount of nitrite and molybdate salt to be diluted in RO water to obtain a concentrated solution of nitrite or molybdate.

$$C_1V_1 = C_2V_2$$

$$(C_i)(V_i) + (C_s)(V_s) = (C_f)(V_i + V_s)$$

but :

$$C_s = 0 \qquad so,$$

$$(C_i)(V_i) = (C_f)(V_i + V_s)$$

where:

C_i = concentration of inhibitor solution, mM
C_s = concentration of inhibitor in liquid manure sample, mM
C_f = final inhibitor concentration desired in the resulting mixture, mM
V_s = volume of liquid manure sample, mL
V_i = volume of inhibitor solution to be applied, mL

Example computation for determining the amount of concentrated nitrite or molybdate solution to obtain their final concentration in the manure:

- To obtain a final concentration of 2 mM nitrite with the use of 200 mM concentrated nitrite solution:

$$(200)V_i = (2)(V_i + 30)$$

$$V_i = 0.304\,mL$$

B. Supplementary experimental data

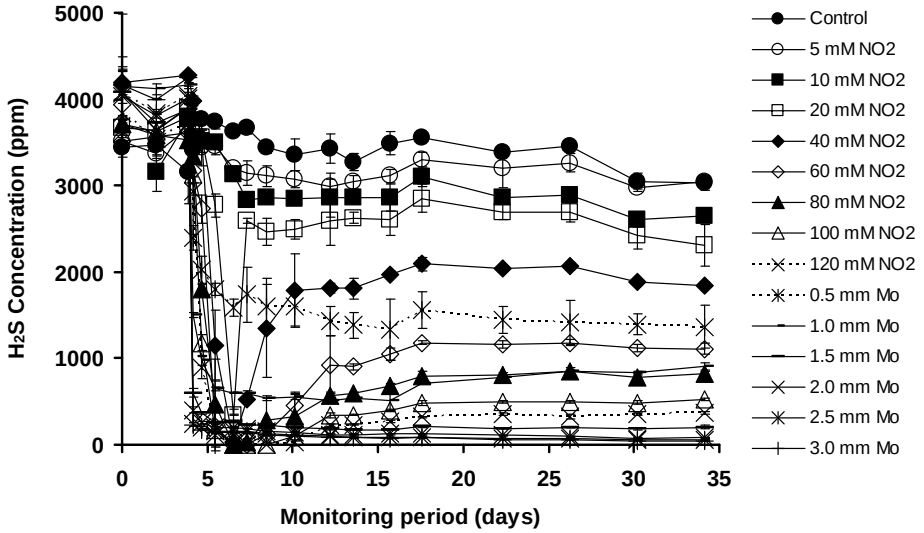

Figure B.1. Profiles of H_2S concentration in the headspace gas of serum bottles containing 1-month old manure treated with various amounts of nitrite and molybdate.

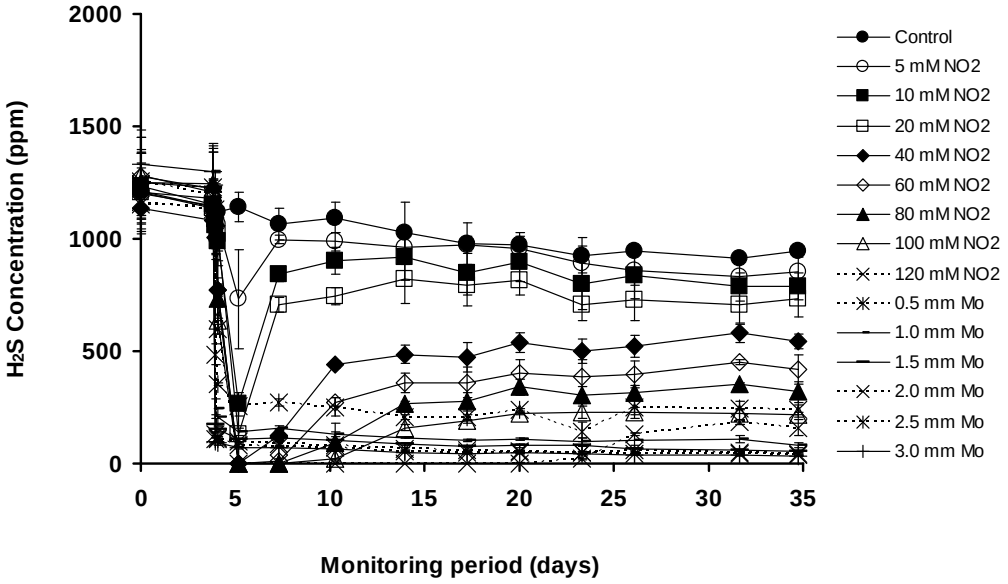

Figure B.2. Profiles of H_2S concentration in the headspace gas of serum bottles containing 3-month old manure treated with various amounts of nitrite and molybdate.

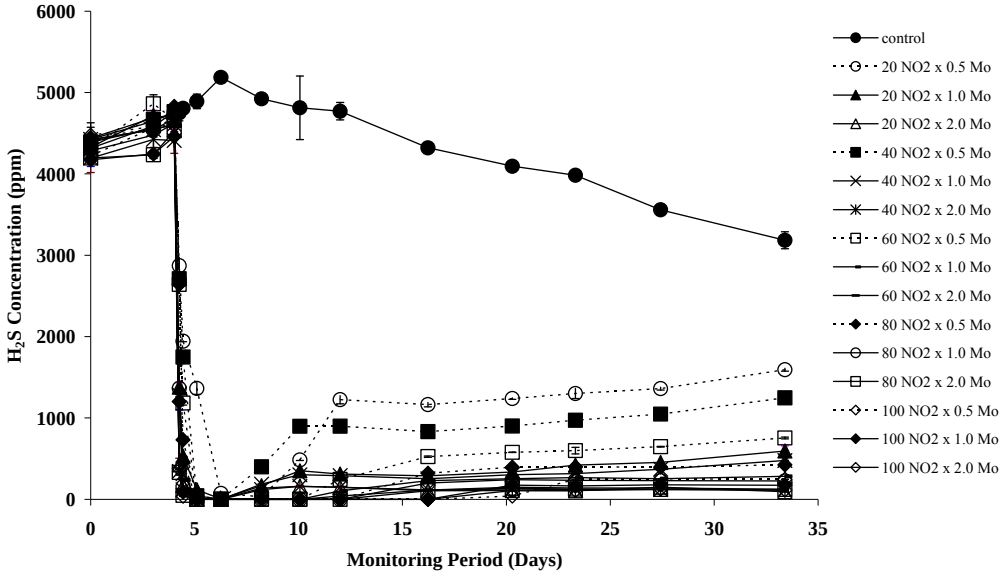

Figure B.3. Profiles of H_2S concentration in the headspace gas of the serum bottles containing fresh manure treated with various amounts of nitrite and molybdate added simultaneously.

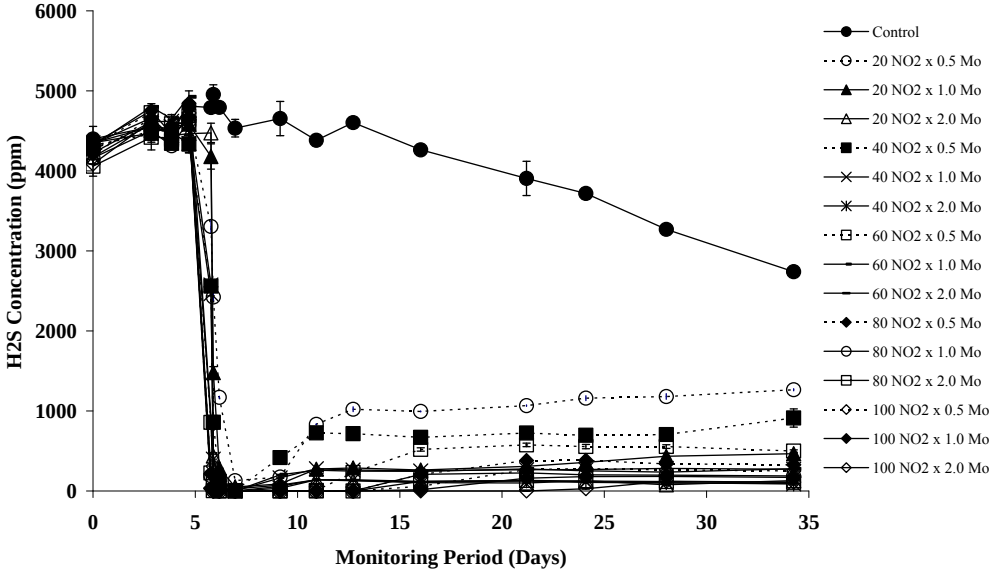

Figure B.4. Profiles of H_2S concentration in the headspace gas of the serum bottles containing fresh manure treated with various amounts of nitrite and molybdate added subsequently.

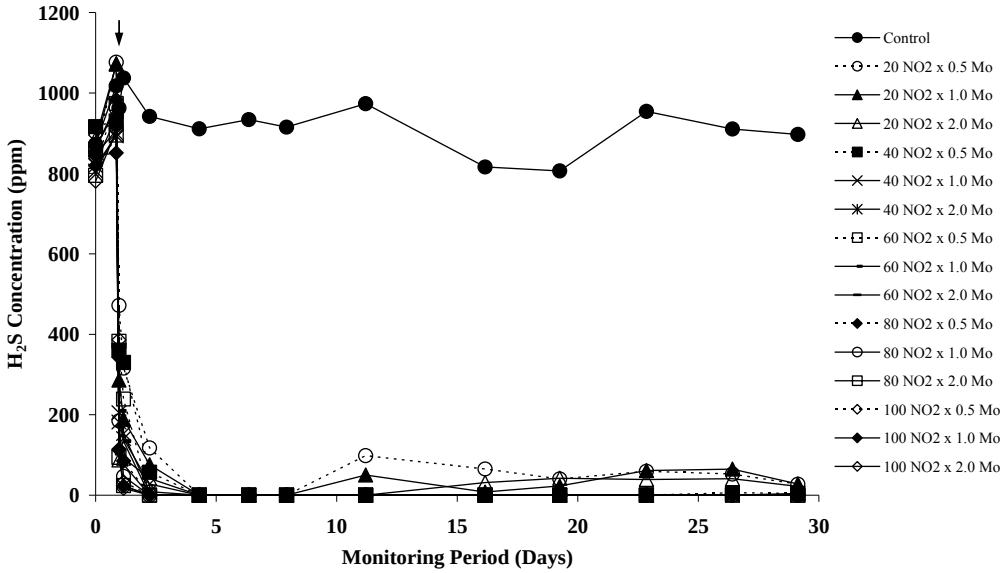

Figure B.5. Profiles of H_2S concentration in the headspace gas of the serum bottles containing 3-month old manure treated with various amounts of nitrite and molybdate added simultaneously.

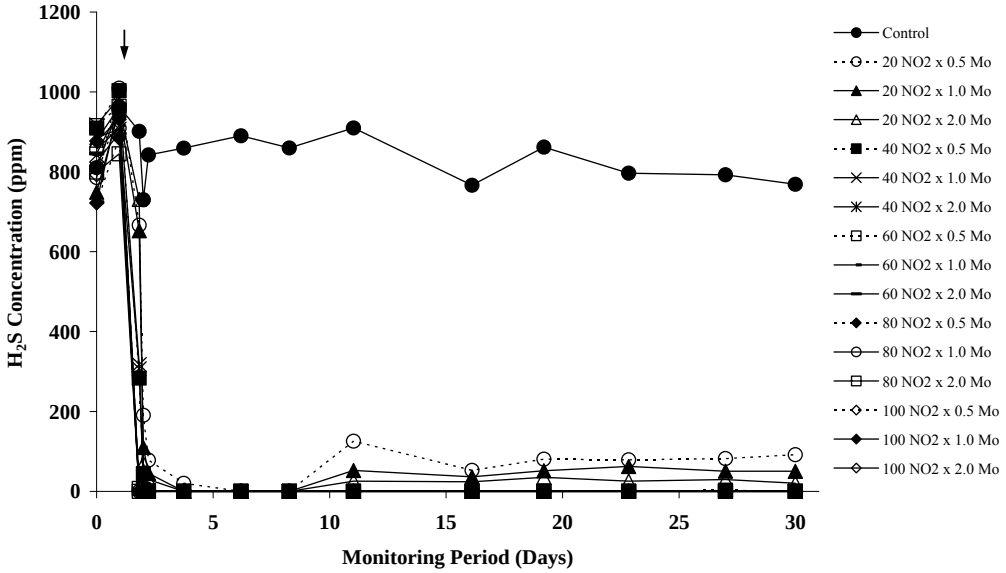

Figure B.6. Profiles of H_2S concentration in the headspace gas of the serum bottles containing 3-month old manure treated with various amounts of nitrite and molybdate added sequentially.

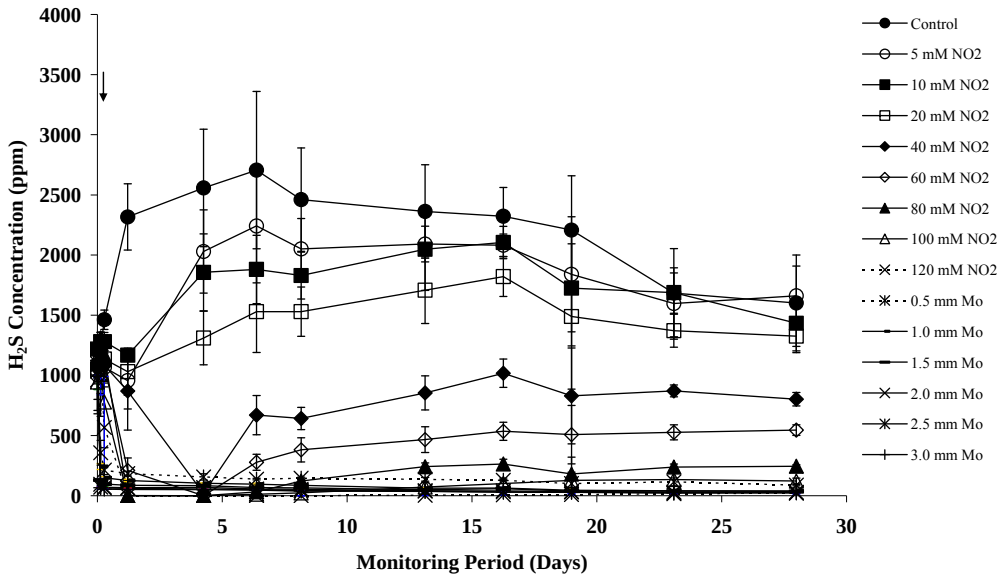

Figure B.7. Profiles of H_2S concentration in the headspace gas of the serum bottles containing fresh manure applied with various amounts of nitrite and molybdate at the beginning.

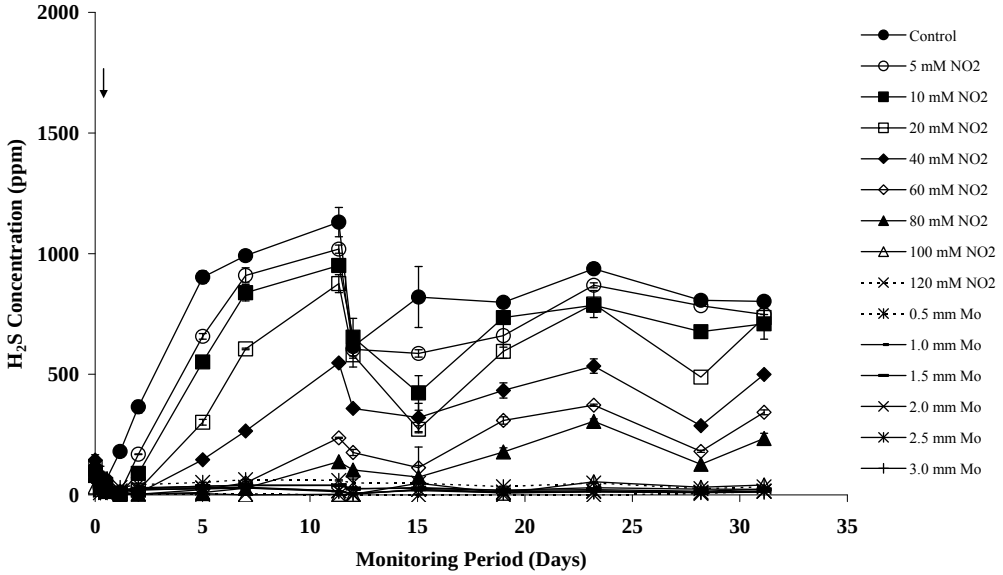

Figure B.8. Profiles of H_2S concentration in the headspace gas of the serum bottles containing 3-month old manure applied with various amounts of nitrite and molybdate at the beginning.

Table B.1. Concentrations of H_2S in the control and treated chambers obtained from the different sampling levels at 10 and 15 minutes after manure agitation during the second trial.

Sampling elevation	Control		Treated	
	10 Minutes	15 Minutes	10 Minutes	15 Minutes
Pit	2.26	0.40	0.40	0.40
Animal	0.96	0.43	0.40	0.40
Human	1.11	0.40	0.40	0.40
SD				
Pit	0.29	0.00	0.00	0.00
Animal	0.25	0.00	0.00	0.00
Human	0.20	0.00	0.00	0.00

Table B.2. Concentrations of H_2S in the control and treated chambers obtained from the different sampling levels at 10 and 15 minutes after manure agitation during the second trial.

Sampling elevation	Control		Treated	
	10 Minutes	15 Minutes	10 Minutes	15 Minutes
Pit	0.85	0.40	0.61	0.40
Animal	0.60	0.40	0.31	0.40
Human	0.61	0.40	0.35	0.40
SD				
Pit	0.22	0.00	0.11	0.00
Animal	0.08	0.00	0.05	0.00
Human	0.12	0.00	0.09	0.00

C. Feasibility study calculation details

Table C.1. Operational details and information used in the cost estimation for control of H_2S emission with molybdate applied in a complete growth cycle in a grow-finish room.

	Week	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
A*	Days	0	7	14	21	28	35	42	49	56	63	70	77	84	91	98	105	112
	Pit pulling					1			2		3		4		5		6	
B	Number of pigs per room	72																
C	Weight per pig throughout growth period, kg	20	26.3	32.6	38.9	45.2	51.5	57.8	64.1	70.4	76.7	83	89.3	95.6	102	108	115	121
D	Manure production rate (L/day)																	
D_1	30-68 kg	2.27																
D_2	68-90 kg	6.36																
E	Manure pit volume produced per pig, L	0	15.9	31.8	47.7	63.6	15.9	31.8	47.7	44.5	89.0	44.5	89.0	44.5	89.0	44.5	89.0	133.6
F	Manure pit volume per room, L	0	1144	2288	3432	4576	1144	2288	3432	3205	6411	3205	6411	3205	6411	3205	6411	9616
	Treatment cost																	
	Treatment application				X			X		X		X		X		X		
	Time interval between two consecutive treatments (days)				21			21		14		14		14		14		
G	Final treatment concentration in manure, mM	0.1																
H	Concentration of treatment solution, mM	20																
I	Volume of treatment solution to be applied, L				23.0 0			17.2 5		32.2 2		32.2 2		32.2 2		48.3 2		
J	Total volume of treatment solution per room, L	185.2																
K	Total amount (kg Mo) per room	0.896																
L	Molybdate price, $/kg	**$ 41.28**																
	Base price ($/kg) 35																	
	Minimum purchase (90 kg) 3150																	
L_1	With Tax 3465																	
L_2	Shipping 250																	
M	Molybdate cost ($) per room	**$ 37.0**																
N	Molybdate cost ($) per finished pig	**$ 0.51**																

Table C.1. cont'd

	Labour cost		
	Number of hours to apply each treatment	0.5	
	Number of hours to apply treatment per cycle	3	
O_1	Labour cost per cycle, $	39	
	Labour cost per hour, $/hr	13	
O	Labour cost per pig per cycle, $		**$ 0.54**
	Material and capital cost		
	Backpack sprayer		$ 150
	Weighing balance		$ 150
	75-L Containers @ $15 each		$ 60
P	Total		$ 360
Q	Estimated equipment lifespan, yr		5
R	Cost per pig per yr		**$ 1.00**

* Letters are notations used for equations list (Table C.3)

Table C.2. Estimation of molybdate cost for a 300-sow barn grow-finish operation.

S*	Number of finished pigs per year (25 pigs per sow per year)		7,500
T	Molybdate cost for treating finishing pigs per yr, $/yr		3,854.5
U	Labour cost per year, $/yr		4,062.5
V	Capital Cost per year, $/yr		72
V_1	Cost per pig per yr, $	0.01	
W	Total cost, $		$7,988.96
X	Cost per finished pig per year, $/pig/yr		**$ 1.07**

* Letters are notations used for equations list (Table C.3)

Table C.3. List of working equations used for the estimation of molybdate cost for a grow-finish pig operation.

C	= 20 + 0.9 x A	O	$= O_1/B$
E	if { C<68, $= D_1 \times (A_{\text{during pit pulling}} - A_{\text{initial}})$; C>68, $= D_2 \times (A_{\text{during pit pulling}} - A_{\text{initial}})$	R	= P/Q/B
F	= B x E	T	= S x N
I	= G x F/(H - G)	U	= S x O
J	= sum(I)	V	$= V_1 \times S$
K	See Appendix A	V_1	= P/Q/S
L	$= (L_1 + L_2)/90$	W	= T + U + V
M	= K x L	X	= W/S
N	= M/B		